

UNCLASSIFIED

AD NUMBER
AD066774
NEW LIMITATION CHANGE
TO Approved for public release, distribution unlimited
FROM Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; Jul 1955. Other requests shall be referred to Wright Air Development Center, Wright-Patterson AFB, OH. 45433.
AUTHORITY
AFWAL ltr, 17 Apr 1980

THIS PAGE IS UNCLASSIFIED

WADC TECHNICAL REPORT 55-190

PART I

AD0066774

OFFICIAL FILE COPY

D113

**DEVELOPMENT AND EVALUATION
OF A GREASE FOR -100°F TO $+350^{\circ}\text{F}$**

ERNEST W. NELSON

WARREN W. WOODS

C. RICHARD BERGEN

BILLY P. SCOTT

RICHARD M. TILLMAN

CONTINENTAL OIL COMPANY

JULY 1955

WRIGHT AIR DEVELOPMENT CENTER

20040223110

BEST AVAILABLE COPY

NOTICES

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

- - - - -

Qualified requesters may obtain copies of this report from the ASTIA Document Service Center, Knott Building, Dayton 2, Ohio.

- - - - -

Copies of WADC Technical Reports and Technical Notes should not be returned to the Wright Air Development Center unless return is required by security considerations, contractual obligations, or notice on a specific document.

**DEVELOPMENT AND EVALUATION
OF A GREASE FOR -100°F TO +350°F**

*ERNEST W. NELSON
WARREN W. WOODS
C. RICHARD BERGEN
BILLY P. SCOTT
RICHARD M. TILLMAN*

CONTINENTAL OIL COMPANY

JULY 1955

MATERIALS LABORATORY
CONTRACT No. AF 33(616)-2364
PROJECT No. 3044

WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

FOREWORD

This report was prepared by Continental Oil Company under USAF Contract No. 33(616)-2364. This contract was initiated under Project No. 3044, "Aircraft Lubricating Greases", Task No. 73310, "Wide Temperature Range Grease", formerly RDO No. 613-11, "Aircraft Lubricating Greases", and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Mr. H. Schwenker acting as project engineer.

This report covers work done from 15 March 1954 to 15 March 1955. Future reports will be prepared as the work progresses.

ABSTRACT

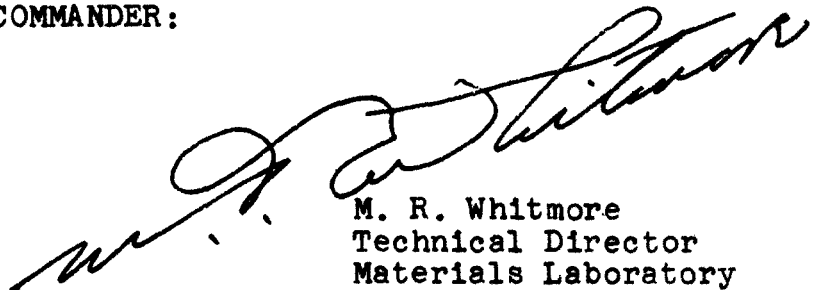
This report describes the history and present status of the development of a general purpose grease to be operational over a -100°F. to $+350^{\circ}\text{F.}$ temperature range. Experimental work has been conducted during the past 12 months by Continental Oil Company under AF 33(616)-2364 and is to be continued under a nine-month extension contract.

These studies have been limited to development of greases thickened by colloidal calcium carbonate coated with calcium salts of aliphatic dicarboxylic acids. Using diester vehicles, it now appears probable that a balanced formulation can be made which will meet specifications for consistency, bleeding, work stability, dropping point, evaporation loss, low temperature torque, and water resistance. Some revision in composition of present greases will be required since incorporation of work stability and water resistance additives has been found to induce changes in consistency and bleeding which must be offset by slight changes in the thickener. In addition, an oxidation inhibitor must be incorporated prior to starting prolonged bearing tests at high temperatures.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



M. R. Whitmore
Technical Director
Materials Laboratory
Directorate of Research

TABLE OF CONTENTS

	Page
INTRODUCTION.	vii
SELECTION OF BASE OILS.	1
Literature Studies of Possible Types	1
Silicone Fluids.	2
Silicate Esters.	4
Aliphatic Diesters	5
SELECTION OF DISPERSING AGENT	7
SELECTION OF COUPLING AGENT	9
THIXOTROPY PROBLEM.	11
SET PROBLEM	14
FORMULATION OF AN OPTIMUM GREASE.	17
APPENDIX I - Solubility of Various Materials at 10 Per Cent in DC 200-100 cs.	20
II - Details of Grease Preparation	23
III - Small Sample Evaluation of Pluroxin E 231 Greases	24
IV - Small Sample Evaluation of 3 Methyl Glutaric Acid Greases	25
V - 3 Methyl Glutaric Acid Greases.	26
VI - Materials Ineffective as Thixotropy Inhibitors.	29
VII - Effect of Additives on 3 Methyl Glutaric Acid Coupled Greases	30
VIII - Effect of Finishing Temperature on Grease Properties	31
IX - Unsuitable Set Inhibitors	32
X - Exhibit "A"	33

LIST OF ILLUSTRATIONS

	Page
FIGURE I - Effect of Particle Size on Worked Stability.	35
II - Effect of DC 510 Silicone Fluid on Worked Stability	36
III - Effect of Varying Per Cent Active Gelling Agent and Per Cent Silicone at a Constant Dispersion Ratio (0.2) .	37
IV - Effect of Varying Per Cent Active Gelling Agent and Per Cent Silicone at a Constant Dispersion Ratio (0.3) .	38
V - Effect of Varying Per Cent Active Gelling Agent and Per Cent Silicone at a Constant Dispersion Ratio (0.35). .	39
VI - Effect of Varying Per Cent Active Gelling Agent and Per Cent Silicone at a Constant Dispersion Ratio (0.4) .	40
VII - Effect of Varying Per Cent Active Gelling Agent and Per Cent Silicone at a Constant Dispersion Ratio (0.45). .	41
VIII - Effect of Varying Per Cent Active Gelling Agent and Per Cent Silicone at a Constant Dispersion Ratio (0.5) .	42
IX - Dispersion Ratio - Active Gelling Agent Requirements for 300 Penetration Grease.	43
X - Effect of Varying Per Cent Acryloid and Per Cent Silicone on a Constant Active Gelling Agent (8 Per Cent) and Dispersion Ratio (0.3) Grease.	44
XI - Effect of Varying Per Cent Acryloid and Per Cent Silicone on a Constant Active Gelling Agent (8 Per Cent) and Dispersion Ratio (0.4) Grease.	45

LIST OF ILLUSTRATIONS (CONTINUED)

	Page
FIGURE XII - Effect of Acryloid and Esso Acto on a 0.4 Dispersion Ratio, 9 Per Cent Active Gelling Agent, 10 Per Cent Silicone Grease.	46
XIII - Variation of a 0.4 Dispersion Ratio, 8.5 Per Cent Active Gelling Agent Grease as a Function of the Molecular Weight of the Sulfonate Dispersant. .	47

INTRODUCTION

In the past few years it has become apparent that the ever increasing temperatures encountered in air frame mechanisms make a universal grease unlikely. As a result of these higher temperatures, it has become necessary to go to special vehicles of high oxidative resistance and low volatility. Generally, such a change has meant sacrificing low temperature performance. Universally, it has meant a marked increase in vehicle and thickener cost. Consequently, there has been increasing interest in developing two distinct types of greases, namely:

- (1) A relatively cheap grease capable of service from exceedingly low to moderately high temperatures which might suffice for the bulk of the applications.
- (2) A grease capable of service at extremely high temperatures, compromising low temperature performance if necessary.

The work described in this report concerns development of the first type of grease. Target requirements are for service over a -100°F. to $+350^{\circ}\text{F.}$ temperature range.

In studies prior to acceptance of this contract, Continental Oil Company was exploring properties of petroleum base greases thickened with colloidal calcium carbonate which had been coated with calcium salts of dibasic aliphatic acids. These greases exhibited exceptionally high dropping points. While petroleum oils would not be suitable vehicles for -100°F. to $+350^{\circ}\text{F.}$ grease, it was thought that such thickeners could be advantageously used in synthetic vehicles, such as diesters, silicate esters, and silicones.

Thickeners of this type require a special mode of preparation, regardless of the vehicle used. Basically, a colloidal dispersion of calcium carbonate is prepared in situ in the vehicle in appropriate solvents. Dispersing agents are necessarily present during the carbonate formation in order to obtain sufficiently small particle sizes. A dicarboxylic acid is then added to the dispersion and reacts partially with the calcium carbonate particles. Removal of solvents then produces the thickened grease.

A number of special terms are used to describe such a preparation in shorthand fashion. These include:

- (1) Dispersion ratio = $\frac{\text{weight calcium carbonate}}{\text{weight dispersing agent}}$

- (2) Active gelling agent = Weight per cent of the final grease consisting of calcium carbonate plus calcium salt of the dibasic acid
- (3) Conversion = Weight per cent of original calcium carbonate which has been converted to calcium salt of the dibasic acid
- (4) Intermediate = calcium carbonate dispersion prior to addition of dibasic acid
- (5) Coupling agent = dibasic acid used for reaction with calcium carbonate

In practice, it is convenient to prepare colloidal calcium carbonate starting from a slurry of lime in methyl alcohol. This slurry is blown with hydrogen sulfide, thus producing a solution of calcium sulfhydrate in methyl alcohol. This solution is then added to a solution of the dispersing agent in the vehicle and/or additional solvents such as benzene or naphtha. The resultant blend is then blown with carbon dioxide, releasing hydrogen sulfide and forming colloidal calcium carbonate. If the vehicle involved is sensitive to strong base, it can be added after carbonating rather than earlier. Solvent stripping then results in the intermediate. Usually these intermediates are prepared as concentrates which are diluted as desired with additional vehicle or solvents prior to grease formation. If properly made, they are optically clear, viscous liquids with particle size less than 0.2 micron.

In applying the foregoing method of thickener preparation to vehicles suitable for a -100°F. to $+350^{\circ}\text{F.}$ operation, it was anticipated that major changes in coupling agent and formulation might be required. The proposed plan of attack was therefore staged as follows:

1. Selection of base oil
2. Extensive bench testing to determine the best dispersing agent and coupling agent types.
3. Preparation and testing of optimum grease formulations with oxidation inhibitors, waterproofing agents, etc., incorporated as needed.

SELECTION OF BASE OILS

Literature Studies of Possible Types

A rather extensive literature survey was made at the beginning of this project aimed primarily at selection of the best base oil from the thermal standpoint. Chief considerations were oxidation and volatility at high temperature (e.g., 350°F.) and viscosity in the vicinity of -100°F. Another important consideration was that of solubility of commonly used dispersing agents and additives.

The viscometric properties of conceivable carriers indicate that the best general type of base oil would be a silicone. The silicones have, however, been found to be relatively poor lubricants and even poorer solvents. Both lubricity and solvency can be improved by blending in twenty per cent or more of an aliphatic diester. This of course limits the utility of the blend to the thermal stability of the diester employed. At the onset of this program, leading manufacturers of applicable silicones were approached for information regarding solubility of polar materials in their fluids. None could indicate a suitably soluble and effective dispersing agent for calcium carbonate.

The silicate esters were a second possibility for base oils. These materials were indicated to have excellent thermal viscosity relationships and are relatively stable to oxidation below 500°F. Many are prone to hydrolysis in the presence of water, however; and thermal decomposition products are indicated to include abrasive silica particles. Certain recently developed esters of disilicic acid, however, have been found adequately stable to hydrolysis and to be resistant to final breakdown to abrasive material. Furthermore, these silicate esters are much better solvents for known dispersing agents than are the silicones.

The literature studies also indicated that certain aliphatic diesters are possible candidates either in blends with silicones or alone. These diesters have the advantage of much lower cost than either silicones or silicate esters. Their structure, furthermore, is such that they should be relatively good solvents for customary dispersants. Table I shows thermal properties for some diesters of particular interest as given by listed authorities.

TABLE I - ALIPHATIC DIESTERS

	<u>Pour Point</u>	<u>Flash Point</u>
di-2,ethyl hexyl sebacate (1)	-67°F.	450°F.
di-2,ethyl hexyl azelate (2)	-85	445
di-2-ethyl hexyl adipate (3)	-100	395
di-2,ethyl propyl azelate (1)	below -108	380
di-2,ethyl butyl azelate (2)	-85	365

- (1) Ind. Eng. Chem., Volume 39 (1947), page 500.
- (2) Physical Properties of Plastolein 9050 and 9058, Emery Industries.
- (3) Georgi, C. W., Motor Oils and Engine Lubrication, page 235, Reinhold, 1950.

The lower temperature limits given are evidently somewhat dependent on method of testing. The di-2,ethyl hexyl azelate for instance was found to have a pour point of around -100°F. in Continental Oil Company laboratories.

The diesters in general possess adequate lubricity. They are prone to hydrolysis in the presence of strong bases but are quite stable in the presence of water alone.

Silicone Fluids

The most promising candidates among the silicone oils appeared to be Dow Corning's DC 510-50 and General Electric's SF 81-40. Infrared analysis of these materials indicated that they were quite similar, being methyl phenyl polysiloxanes of moderate aromaticity. The poly methyl siloxanes (DC 200, DC 500) and the higher aromaticity analogues (DC 550 and DC 710) have pour points which render them unsatisfactory for the contract grease.

Since there was some delay in receiving the most desirable silicone fluids, initial screening for solubility was with DC 200-100. It was thought that any material soluble in the DC 200 would be soluble in the DC 510 with its higher aromatic content. Appendix I lists those materials tested.

The commonly used dispersing agents (e.g., naphthenates and sulfonates) were found to be insoluble. Of the soluble materials only the higher molecular weight amines and fatty acids were believed to hold any promise as dispersing agents.

Using the general procedure outlined in the introduction, two materials found soluble in the above tests, namely

pelargonic acid and phenyl acetic acid, were tested for their ability to disperse calcium carbonate in DC 510-50. Gel formation occurred with both materials, and products appeared gritty due to large particles of calcium carbonate. They were obviously unsuited for use as grease intermediates.

It became increasingly clear that silicone alone did not have adequate solvency; hence blends incorporating aliphatic diesters were used for further study. (This also would be expected to improve the lubricity of any greases developed.) A third promising material (di-2,ethyl hexyl amine) was therefore tested in a blend of 20 per cent di-2,ethyl butyl azelate and 80 per cent DC 510-50 silicone fluid. This amine, although somewhat volatile at the finishing temperature (150°C.), formed an optically clear dispersion which was a soft gel at room temperature. No particles were visible in a bright field microscope even at 1350 X magnification. Particles were, however, too large to form a grease even though some thickening did occur upon the addition of a coupling agent.* In view of very unsatisfactory performance of pelargonic and phenyl acetic acids in undiluted silicone, these materials were not further tested in the silicone-diester blend.

Certain naphthenic acids (Eastman P2388 and several Oronite products) were found to be soluble in a 50:50 blend of DC 510-50 and di-2,ethyl hexyl azelate; but again attempts to form dispersions failed, although a number of procedure variations were utilized.

It appeared at this stage that the silicone molecule itself offered the best possibility for a suitably soluble dispersing agent, provided suitable polar groups could be introduced therein. The most preferable polar groups were thought to be carboxyl, sulfonate, or amine. Accordingly, deliberate attempts to introduce these groups were made.

A first attempt at sulfonation used a stabilized liquid sulfur trioxide. It was found to cause scission of the silicon-phenyl bonds. Other standard sulfonating agents likewise were unsatisfactory.

Attempts at halogenation with HCl in glacial acetic caused degradation of the silicone polymer. Direct photochlorination resulted in introduction of a chlorine in the methyl groups. This chlorine was not sufficiently reactive to allow introduction of sulfonic or carboxylic groups by the usual methods. Amines were, however, prepared by blowing the chlorinated intermediate with ammonia. When used as dispersing agents, these amines were subject to thermal desorption and allowed coagulation and precipitation of the calcium carbonate.

*Pluroxin E231. See section on coupling agents for description.

At this point, efforts to use silicone fluids as primary base oils were abandoned; and work was begun on alternate base oils.

Silicate Esters

The alkyl aryl sulfonate dispersing agent used previously in hydrocarbon systems is adequately soluble in certain silicate esters and has been found to function normally therein. One silicate ester was extensively tested. This material, known as MLO 8200, is a compounded hydraulic fluid. Composition is predominantly hexa (2 ethyl-butoxy) disiloxane along with 4.8 per cent XF 371 (100,000 cs.), 2 per cent p,p' dioctyl-diphenyl amine, and 0.02 per cent quinizarin. This material had a pour point below -102°F. and was indicated to be stable at 350°F.

Since this material was sensitive to strong base, a transfer technique was used in preparing the intermediate. This consisted of preparing the dispersion in volatile solvents and adding the base oil only after the sulfhydrylate had been converted to the less reactive carbonate. The intermediate was then stripped of solvents in the usual fashion. No noticeable hydrolysis of the silicate ester occurred, and products proved to be good dispersions with one drawback. The MLO 8200 was a compounded oil, and intermediates made therefrom tended to separate. The upper layer was believed to be predominantly XF 371 polymer plus some silicate ester. At higher dispersion ratios more of the silicate ester was driven into the upper layer. Below in Table II are listed the intermediates along with pertinent data.

TABLE II - SILICATE ESTER INTERMEDIATES

<u>Experiment No.</u>	<u>Base Oil</u>	<u>Dispersion Ratio</u>	<u>Base No.</u>	<u>Per Cent Calcium</u>
CRB 4-23	MLO 8200	0.285	80	5.0
CRB 4-26	MLO 8200	0.385	100	8.9
CRB 4-27	MLO 8200	0.546	108	9.1

Greases were prepared from each of the above intermediates using Pluroxin E 231 (see section on coupling agents for description) as the coupling agent. Table III lists some of these greases showing consistency and melting points. Certain of these greases did not show appreciable separation even after several months' storage.

TABLE III - SILICATE ESTER GREASES

<u>Experiment No.</u>	<u>Based on Intermediate</u>	<u>Per Cent Active Gel- ling Agent</u>	<u>Per Cent Worked Con- version</u>	<u>Pene- tration</u>	<u>Dropping Point</u>
CRB 4-24	CRB 4-23	7	70	*	above 437°F.
CRB 4-25	CRB 4-23	4	70	230	374°F.
CRB 4-28	CRB 4-27	4	50	320	373°F.

*Too heavy to work.

Silicate esters were not available in sufficient quantities for further study at that time; so work was switched to the aliphatic diesters as per letter from the project engineer.

Aliphatic Diesters

The aliphatic diesters are good solvents for known mineral oil soluble dispersing agents. In fact, prior mineral oil experience was found to be directly applicable in general to the aliphatic diesters. Colloidal dispersions of calcium carbonate using certain naphthenic and alkyl aryl sulfonic acids were readily made in various diesters. These intermediates appeared to have particle sizes of requisite smallness. Two examples are given in Table IV. These dispersions were optically clear and stable to centrifuging and moderately long storage.

TABLE IV - STABLE DIESTER INTERMEDIATES

<u>Experiment No.</u>	<u>Base Oil</u>	<u>Dispersion Ratio</u>	<u>Base No.</u>	<u>Per Cent Ca</u>	<u>Dispersing Agent</u>
CRB 4-2	Di-2,ethyl butyl azelate	0.24	121	7.0	Sulfonate
BPS 2-47	Di-2,ethyl hexyl azelate	0.44	199	7.9	Naphtenate

It was thought that di-2,ethyl hexyl azelate would be the best choice among the diesters. This material has a relatively high flash point suggesting a minimum of oxidation and volatilization in the vicinity of 350°F. A standard oxidation inhibitor such as phenothiazine should inhibit oxidation sufficiently to meet specifications. At the same time di-2,ethyl hexyl azelate has a lower pour point than other high molecular weight diesters and should give greases more likely to meet the low temperature specifications.

There was some initial speculation about the hydrolytic and pro-oxidative effects of the rather large surface area of calcium carbonate presented to the diester. Since in the grease the calcium carbonate is shielded by the inert coupling agent salt, it was expected that little or no trouble of this nature would occur. This supposition has been confirmed by the low evaporation actually exhibited by such greases (see Appendix IV).

With the selection of di-2,ethyl hexyl azelate as the developmental base oil, work went ahead on discovering the better dispersing and coupling agents. Since there was some delay in receiving sufficient quantities of the preferred diester, some of this work was performed with other diesters; however, since the applicable physical properties of the various diesters are quite similar, it was believed the particular diester employed for this initial screening was immaterial.

SELECTION OF DISPERSING AGENT

The dispersing agent is primarily used to aid in the formation of colloidal particles of calcium carbonate. These particles are, of course, formed during the carbonation step of the grease intermediate preparation. In this stage, the dispersant is adsorbed on the surface of the particles and prevents agglomeration. It also serves to inhibit normal crystal growth.

The smaller the inorganic particle size the more efficient a thickener it becomes per unit weight. Since during addition of the coupling agent the ultimate particle size is greatly increased, it has been found that there is an upper limit of 0.2 micron diameter above which satisfactory greases cannot be made. To a certain extent, dispersion ratio is an indication of particle size, since increasing amounts of sulfonate tend to increasingly inhibit crystal growth.

Since a substantial amount of dispersing agent is required in general to give the requisite particle size, it is present in the final grease to an extent which has an appreciable effect on the grease properties. An upper limit is set by the tendency of the dispersing agent to fluidize the grease gel. With alkyl aryl sulfonates, this upper limit lies in the vicinity of 0.3 dispersion ratio and the lower limit around 0.45. It should be noted that dispersion ratio indicates not only particle size but also is used to show dispersion agent level in the final grease.

A representative naphthenic acid and several sulfonic acids were tested as dispersants in the diesters. Clear fluid dispersions were prepared in di-2,ethyl hexyl adipate utilizing Naphtone "D" (a naphthenic acid supplied by Standard Oil of California) as the dispersing agent. Dispersion ratios in the range of 0.22-0.44 were employed with base numbers up to 200 (Table IV). Particle size was under 0.2 micron. Attempts to prepare greases from these intermediates failed due to coagulation of the dispersion in the presence of solvent (acetone) required for introduction of the coupling agents. A search for a mutual solvent was unsuccessful. This dispersing agent was therefore dropped in favor of alkyl-aryl sulfonic acids which were known to be satisfactory dispersing agents in hydrocarbon systems studied prior to the acceptance of this contract. The sulfonic acid found most suitable in diester solvent is prepared by sulfonation of 80 per cent postdodecylbenzene. Postdodecylbenzene is a residual by-product obtained by distilling off dodecylbenzene and lighter fractions from the crude alkylation product of benzene and dodecene. It consists of a mixture of dialkylated benzenes. An 80 per cent postdodecylbenzene is the residue remaining after further distillation of postdodecylbenzene to remove the more volatile 20 per cent therefrom. Average molecular weight of this hydrocarbon is around 382.

Sulfonates from the 20 per cent lower molecular weight fractions of postdodecylbenzene were found to be relatively unsuitable as dispersing agents. The greases resulting from use of these dispersants were prone to increasing surface set and were less work stable than the higher molecular weight fractions.

Use of the higher molecular weight fractions of postdodecylbenzene (40 and 60 per cent bottoms) showed no significant improvement over the normal 80 per cent bottoms fraction in reducing particle size of finished grease.

In order to obtain the optimum intermediate formulation from a standpoint of particle size, the effect of various dispersion ratios was studied. A series of intermediates were prepared with dispersion ratios of .20, .38, .35, .40, and .50 which gave calcium postdodecylbenzene sulfonate contents of 42 to 17 per cent by weight in the intermediate. The effect of increasing sulfonate content in reducing particle size is shown in illustrations I, II, and III. No significant further improvement was noted at dispersion ratios below 0.40.

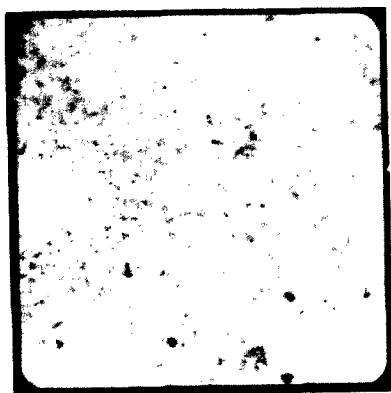


Illustration I
DR = .4



Illustration II
DR = .45

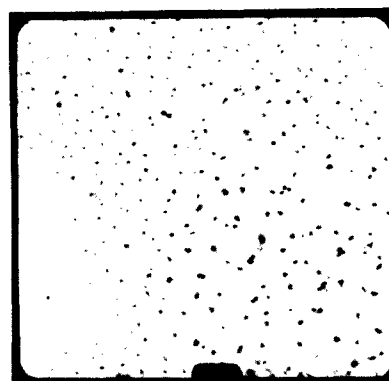


Illustration III
DR = .5

Magnification - 5000 X in each case

SELECTION OF COUPLING AGENT

Coupling agents are dicarboxylic acids which, when added to the grease intermediate (usually with appropriate solvents), react with the colloidal calcium carbonate forming the calcium salts which are required to be insoluble in the base oil. The coupling agents are added in an amount less than required to react with the total calcium carbonate. The function of this calcium salt of the coupling agent is to form a surface on the inorganic particles which causes association of the particles. This association results in a scaffolding gel structure entrapping the base oil thus forming the grease. It is evident that the properties of the grease are markedly dependent on the properties of the coupling agent employed.

In experiments with petroleum greases performed prior to acceptance of this contract, two materials were found to possess outstanding coupling agent properties. These were Pluroxin E 231 (a dicarboxylic acid derivative of polyethylene glycol having a molecular weight of 231) and 3 methyl glutaric acid. It was believed that these materials would behave similarly in di-2,ethyl hexyl azelate inasmuch as the calcium salts of the above acids are substantially insoluble in nearly all high boiling solvents.

A number of grease-like materials were prepared with Pluroxin E 231 as the coupling agent. For the detailed procedure followed in these grease formulations, see Appendix II. The two esters used in the evaluation of Pluroxin E 231 were di-iso-octyl azelate and di-2,ethyl hexyl adipate. The Pluroxin E 231 was found to be effective as a thickener; but in all cases, the resultant grease-like materials bled badly, particularly on working.

Several variations were attempted (see Appendix III) aimed at solving this problem. Per cent conversion was varied from 40 to 70 per cent, which gave materials ranging from viscous liquids to very heavy gels. In all cases, bleeding was excessive at room temperature. The melting point of these Pluroxin thickened greases was below 300°F. which was apparently due to excessive bleeding rather than softening of the gel structure.

Three methyl glutaric acid was then evaluated as a coupling agent. This coupling agent formed grease-like products which did not suffer from bleeding at room temperature nor did they require milling as did the Pluroxin coupled greases. In general, simple stirring was sufficient to cause formation of a buttery texture. Physical characteristics of these 3 methyl glutarate greases are listed in Appendix V. It can be seen that the specifications are very nearly met even

by these early experimental greases. Dropping points are well above 450°F. while only 375°F. is required. Approximately 85 per cent conversion of the total calcium carbonate is optimum versus 40 to 50 per cent optimum found with Pluroxin coupled greases (see Appendix IV). These greases were also found to lack work stability and showed a marked tendency to a work reversible hardening on storage. Despite these disadvantages, the 3 methyl glutaric acid coupled greases were thought sufficiently promising to justify development work to eliminate their deficiencies.

THIXOTROPY PROBLEM

In testing the work stability of the 3 methyl glutarate greases, it was observed that they became semifluid during the 100,000 strokes; but on standing, they reformed to their original consistency. This showed that the breakdown of the grease was not due to alteration of the ultimate particles but was instead an example of extreme thixotropy. It was thought that the cause of this thixotropy was probably due to slow reformation of the gel structure when broken down by high rates of shear. The structure is formed by the association of the spherical particles due to short range attractive forces set up between their surfaces. This surface is composed of the calcium salt of the coupling agent, and it is reasonable that the thixotropic behavior will depend on its chemical nature. In addition, the sulfonate dispersant is known to affect fluidity and presumably thixotropic behavior. It was therefore believed that 3 methyl glutarate greases might require only slight modification to eliminate or markedly reduce thixotropy.

The modification first attempted was alteration of the per cent conversion which, although affecting consistency, had no effect on the thixotropy. To alter the chemical nature of the surface, Pluroxin was mixed with the 3 methyl glutaric acid in various proportions. In all cases the resultant grease exhibited the bad bleeding characteristics of the Pluroxin.

It was believed that reducing particle size may affect the work stability by increasing the number of particles per unit weight of gelling agent, thereby increasing the number of particle collisions during a given time interval. The end result would thus be faster reformation of the gel structure. Several attempts were therefore made to further reduce particle size in the intermediate stage.

It was known from previous experience that some dibasic acids served to inhibit crystal growth in processes similar to that used in forming the intermediate. Experimental use of 3 methyl glutaric acid as a crystal growth inhibitor in the intermediate, however, did not effectively reduce the particle size.

Particle size was, however, reduced through the use of a more dilute solution containing 1.8 milliequivalent per gram calcium sulfhydrate rather than the 4.2 milliequivalent per gram base solution previously employed. The electron micrograph in illustration IV shows calcium carbonate particle size obtained with the 4.2 milliequivalent base solution. Illustration V shows the extra fine particles obtained through the use of the more dilute methanolic-calcium sulfhydrate solution. Figure I shows the effect of this modification on improving the work stability of this grease.

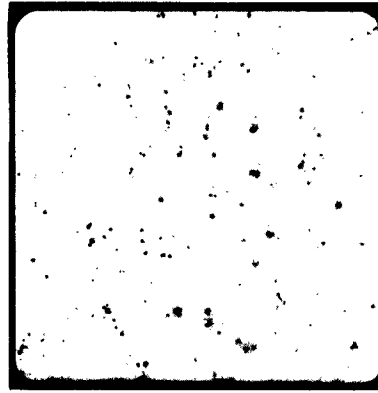
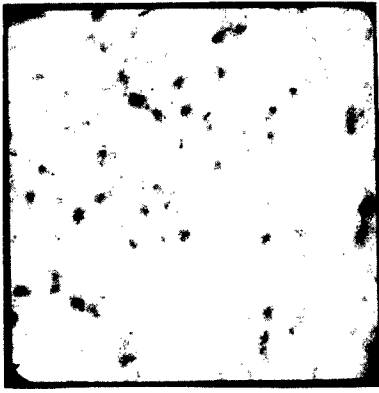


Illustration IV Illustration V
 Normal Intermediate Extra Fine Intermediate
 Magnification -5000X in each case

While this improved grease appeared work stable, several factors had to be studied to obtain the optimum formulation. These factors included dispersion ratio and per cent active gelling agent.

An extensive study was therefore made on the effect of varying dispersion ratios and per cent active gelling agent. From this study, it was found that the worked stability of the grease was a function of the balance between dispersion ratio and per cent active gelling agent (see figures III through VIII). Composition and penetration data on this series of greases are tabulated in Appendix V.

In evaluating the greases prepared at the above dispersion ratios, it is apparent that, at the upper limit of sulfonate concentration (.2 dispersion ratio, 42 per cent sulfonate), the greases are more like viscous liquids and show dropping points in the range of 120°F. At the lower limit of sulfonate concentration (.5 dispersion ratio, 17 per cent sulfonate), the particle size increases, thus requiring a higher per cent active gelling agent to obtain a grease in the useful consistency range (see Figure IX).

Various additives were also evaluated as thixotropy inhibitors. It is known that the characteristics of a given coupling agent vary with the type of vehicle in which it is employed; therefore it was believed that the addition of a modifying diluent with the necessary low volatility at high temperatures might inhibit this thixotropy. The materials tested which had no effect are listed in Appendix VI.

Three materials were found which did reduce the shear breakdown of these greases. The materials were (1) polyethylene glycol 400 (Carbide and Carbon Chemical), (2) DC 510-50 cs. silicone fluid (Dow Corning), and (3) Acryloid 710 (a high molecular weight acrylic polymer). The polyethylene glycol 400 material

was only slightly effective and caused excessive bleeding at the levels required to eliminate thixotropy. The DC 510 silicone fluid was quite effective (see Figure II); however these greases were prone to bleed to some extent. The Acryloid 710 material appears to be both effective at low concentrations and less prone to cause bleeding. Bleeding is more severe with either additive at high sulfonate levels. Figures X and XI show the effect of Acryloid and silicone fluid on the grease. Composition and penetration data are tabulated in Appendix VII.

SET PROBLEM

The early 3 methyl glutaric acid coupled greases exhibited a marked tendency towards a work reversible surface hardening or "set." Although the major problem involving surface set of these greases under normal conditions has been largely overcome in recent grease formulations, there is still a tendency toward surface set when said greases are exposed to an atmosphere saturated with water vapor. None of the various additives incorporated to date have any appreciable effect under these conditions. Surface set can usually be detected in as little as four hours' exposure to high humidity.

A number of modifications in procedure and formulation have been investigated with regard to their effect on surface set. One such modification was the use of a higher temperature in finishing the grease. Originally the grease was vacuum stripped to 150°C. to remove volatile solvents. Greases prepared in this manner still had a strong odor of benzene associated with them; and in addition, such greases were very prone to surface set on overnight exposure to atmospheric conditions. It was also noted that the grease hardened and became crumbly when heated to 195°C. When the temperature of the stripping operations is raised to 195°C., the greases no longer have a benzene odor and show less tendency to take an overnight surface set than their lower temperature analogs (see Appendix VIII). Furthermore, the tendency to become crumbly at 195°C. was eliminated. The 195°C. temperature is very close to the upper limit which can be used in this stripping operation, since above this temperature the diester vehicle begins to volatilize.

The molecular weight of the sulfonate used as a dispersing agent in these greases also has an effect on the tendency toward surface set. A slightly lower molecular weight alkyl aryl hydrocarbon (the 20 per cent low molecular weight fraction of postdodecylbenzene) was inadvertently obtained at one point of this investigation, and the greases obtained using sulfonic acid prepared from this material were exceedingly prone to surface set. An investigation of sulfonic acids of higher molecular weights than the normal 80 per cent postdodecylbenzene sulfonate shows no further improvement in lessening surface set. Postdodecylbenzene hydrocarbon was stripped to 60 per cent and to 40 per cent of its original volume, and sulfonic acids were prepared from these hydrocarbons. No appreciable difference in tendency to surface set can be detected between grease prepared from 80 per cent postdodecylbenzene sulfonic acid and the higher molecular weight sulfonates (see Figure XIII).

It was believed that the set observed with these greases was at least partially due to orientation of the sulfonate dispersant into gel structures following the coupling

step. Some possibility existed of adsorbing the freed sulfonate by still further addition of intermediate. When such addition was made, a noticeable reduction of set was observed. The overbased greases, however, showed increased bleeding. Overbasing with naphthenate intermediate did not affect surface set.

A number of additives have been incorporated in these greases to overcome surface set tendencies. The earliest of these additions were hydroxy and ester compounds. Greases modified with these compounds were prone to bleed and, in general, were not work stable (see Appendix IX).

DC 510 silicone fluid was added chiefly as an aid to improving work stability, but in addition it also showed some improvement in surface set characteristics. Another desirable feature obtained with the use of moderately high silicone levels is the increase in dropping point of the grease. This effect is not particularly noticeable except with low dispersion ratio greases. Greases with dispersion ratios above 0.3 have dropping points in the vicinity of 450°F. without any silicone addition. Silicone does have one drawback, however, in that it tends to cloud the greases and to cause bleeding. In general, it was noted that the higher the dispersion ratio (lower sulfonate content) the more silicone could be introduced into the grease without clouding. It is thought that the silicone precipitates the sulfonate in the grease above a certain critical level.

Another additive that gave improvement in surface set tendencies was Esso Acto 630. This is a high molecular weight (479)sodium mahogany sulfonate (Figure XII). One disadvantage is the fluidizing effect of this additive on the base grease. This material must be used in conjunction with a work stability improver due to its dilution effect.

Acryloid 710, an acrylic polymer, has proved to be a promising additive in that it is an effective surface set retarder and, in addition, is a very good work stability improver; however this material also tends to cloud the grease and contributes to bleeding above optimum concentration levels. The Acryloid 710 is effective in lower concentration than silicone fluid (see figures X through XII).

The greases prepared for study of thixotropy versus composition (see preceding section) were also examined for tendency towards surface set. No particular systematic change in tendency to surface set with sulfonate content was noted. If anything, the lower sulfonate containing greases were slightly more prone to surface set. It was noted, however, that, at certain active gelling agent levels, optimum greases were obtained that were notably superior to other members of the same dispersion ratio series, both in surface set and work stability. This

phenomenon can best be seen in figures III through VIII.

The importance of a slight amount of surface set in these greases is doubtful inasmuch as they resume their normal consistencies on mild working. It is also quite probable that the whole phenomenon is related to water resistance of the greases. Greases to which effective water resistance agents have been added have not as yet been evaluated for tendency towards surface set.

FORMULATION OF AN OPTIMUM GREASE

Time has not permitted the preparation and full scale exhibit A testing of an optimum grease formulation. Greases have, however, been made which passed most requirements, with the notable exception of water resistance. Results of tests run on one of these greases (see Appendix VII for others) are listed below along with specification limits:

TABLE VI

A. Formulation of BPS 2-129-4

Dispersion Ratio	0.3
Active Gelling Agent	8 per cent
Conversion	85 per cent
Ca Sulfonate	14 per cent
DC 510-50	8 per cent
Acryloid 710	10 per cent

B. Exhibit A Test Results

<u>Test</u>	<u>Specification</u>	<u>Experimental Result</u>
Dropping Point	Above 375°F.	Above 450°F.
Worked Penetration	260 to 340	265
Water Resistance	a. Not more than 20 per cent b. No cloudiness	a. 63.3 per cent b. Cloudy
Evaporation	Less than 2 per cent	0.44 per cent
Oil Separation	Not more than 5 per cent	5.0 per cent
Worked Stability	Below 375	260*
Low Temperature Torque	5 Seconds Maximum at -100°F.	1.2 seconds

*3000 Double Strokes Only

Exhibit A tests which were not run on this grease are oxidation stability, dirt, copper corrosion, apparent viscosity, gear wear, high temperature bearing test, and humidity corrosion test. The grease was not compounded with an oxidation inhibitor; hence it was not subjected to those tests requiring prolonged exposure to high temperatures. It will be seen, however, that the evaporation loss was well within requirements and that low temperature properties are satisfactory.

As can be seen from Appendix VII, water resistance of the above grease is somewhat poorer than a number of other

greases similarly containing Acryloid or silicone additives. These additives, however, appear to generally reduce water resistance regardless of formulation.

The data in Appendix VII also suggest that incorporation of Esso Acto 630 slightly reduces the deleterious effect of work stability improvers on water resistance. This material is the sodium salt of a mahogany sulfonic acid. Literature studies have indicated that a number of mahogany sulfonates might be effective, particularly as their zinc, aluminum, or cerium salts. In recent experiments, a number of zinc sulfonates have been screened as water resistance additives. The base grease used was a 0.33 dispersion ratio, 8 per cent active gelling agent product of inferior water resistance. Results are shown in Table VII.

TABLE VII

<u>Water Resistance Additive</u>	<u>Per Cent Additive</u>	<u>Per Cent Loss in Washout</u>
None	-	30.8,34.5
Zinc 80 per cent post-dodecylbenzene sulfonate	3	29.5
Zinc Petronate*	3	13.8,15.2
Zinc salt of Emulsol C-10-25**	3	56.8,47.7

* L. Sonneborn & Sons mahogany sulfonic acid

**Emulsol Corporation mahogany sulfonic acid

It appears from the above fragmentary data that water-proofing effectiveness is sharply limited to specific zinc sulfonates. This conclusion, however, is not firm inasmuch as greases made from a repeat preparation of zinc Petronate were not outstanding. It is quite probable that the manner of making the zinc salt is critical. The good values obtained with zinc Petronate, however, do suggest that a balanced formulation can be obtained which will meet specifications.

Prediction of an optimum formulation at this time is hampered by the fact that most of the work stability data was obtained on formulations containing silicones, whereas fragmentary data indicate Acryloid 710 to be preferable both in efficiency and resistance to bleeding. Extrapolation of present data and trends, however, would indicate an approximate optimum composition as follows:

Dispersion ratio	= 0.4
Active gelling agent	= 8.5-9 per cent
Conversion ratio	= 85 per cent
Acryloid 710	= 3-5 per cent
Zinc Petronate	= 3 per cent
Phenothiazine	= 0.5 per cent
(oxidation inhibitor)	
Base oil	= di-2,ethyl hexyl azelate

Present plans call for complete Exhibit A testing of greases having compositions in this general range.

APPENDIX 1

SOLUBILITY OF VARIOUS MATERIALS AT 10 PER CENT IN DC 200-100 CS.

Soluble

Insoluble

A. Alcohols

Tert-butyl alcohol
2-methyl-2-pentane-1-ol
Heptanol-3
N-octanol
Trimethyl cyclohexanol
Di-isobutyl carbinol
Trimethyl nonanol
2-butyl octanol
Tetradecanol
Heptadecanol

Diethyl amino ethanol
2-amino-2-methyl-1-propanol
Tetrahydrofurfuryl alcohol
3-cyclohexene 1-methanol
Dibutyl amino ethanol
2, 3 dihydro -2, 5-dimethyl -1,
4-pyran 2-methanol
Alkyl aryl poly ether alcohols

B. Amines

2 ethyl hexyl amine
N,N, dibutyl isopropanol
amine
Di 2-ethyl hexyl amine

Ethylene diamine
Triethylene tetramine
Monoethanolamine
Ethyl monoethanolamine
Diethanolamine
Phenyl ethanolamine
Triethanolamine
Butyl diethanolamine
Triethylene pentamine
Mixed isopropanolamines
N-methyl glucamine

C. Carboxylic Acids

Butyric acid
2-ethyl hexenoic acid
Pelargonic acid

Stearic acid
Phenyl acetic acid

3-ethyl-3-hydroxy hexanoic acid
Phthalic acid
Polyoxyethylene dicarboxylic
acid, MW = 231
Abietic acid
Anthranilic acid
Naphthenic acids

D. Ethers

Ethylene glycol diethyl
ether
Diethylene glycol diethyl
ether

Poly glycol ethers

APPENDIX 1 (CONTINUED)

SOLUBILITY OF VARIOUS MATERIALS AT 10

PER CENT IN DC 200-100 CS. (CONTINUED)

<u>Soluble</u>	<u>Insoluble</u>
D. <u>Ethers (Continued)</u>	
Ethylene glycol monobutyl ether	
Ethylene glycol di-n-butyl ether	
Diethylene glycol dibutyl ether	
Ethylene glycol monohexyl ether	
E. <u>Esters</u>	
2-ethyl hexyl acrylate	Dibutyl phthalate
Ethyl hexyl acetate	Di (2-ethyl hexyl) phthalate
Di-2-ethyl hexyl tetrahydrophthalate	Poly oxy ethylene esters
	Polymerized high glycol fatty acid esters
	Fatty acid esters of poly ether alcohols
	Sulfate esters of alkyl phenoxy-poly oxy ethylene ethanols
F. <u>Glycols</u>	
	2-ethyl butoxy 2, 4-dimethyl pentanediol-1,5
	2-amino-2-ethyl-1, 3-propanediol
	Dimethyl tetraethylene glycol
	Polyalkylene glycols
G. <u>Ureas</u>	
N,N,N,N tetrabutyl urea	N-mono-n-butyl urea
H. <u>Ketones</u>	
Pentanedione-2,4	
1-phenyl-1, 3-butanedione	

APPENDIX 1 (CONTINUED)

SOLUBILITY OF VARIOUS MATERIALS AT 10

PER CENT IN DC 200-100 CS. (CONTINUED)

Soluble

Insoluble

I. Miscellaneous Organic Compounds

Lactonitrile	Paraformaldehyde
Dimethyl furane	N-vinyl pyrrolidone
Ethylene dichloride	Tris (hydroxy methyl) amino methane
Diethyl furane	Sodium p-xylene sulfonate
	Iso-amyl-2-ethyl-hexyl acid orthophosphate
	Dodecyl benzyl trimethyl ammonium chloride
	Nonyl phenol
	Alkyl aryl sulfonates

SOLUBILITY OF FLUOROCARBONS AT 40 PER CENT IN DC 510-50 CS.

Soluble

Insoluble

Perfluor butyric acid	F-126
Trifluor acetic acid	O- 75
	N- 43
	Calcium perfluor butyrate
	Calcium trifluor acetate

APPENDIX II

DETAILS OF GREASE PREPARATION

Small Sample (100 Grams)

- Step 1 - Weigh out the required amount of grease intermediate dispersion and aliphatic diester into 400-ml. beaker, add 50 ml. benzene, and stir.
- 2 - Weigh out coupling agent into a 150-ml. beaker, dissolve in 50-ml. acetone, and then add 50 ml. benzene.
- 3 - Continue stirring the intermediate solution and slowly add the coupling agent solution over a 15 to 30-second period. Allow 30 to 60 seconds for reaction while stirring is continued.
- 4 - Strip solvents (acetone and benzene) to 150°C. Agitation is mandatory in order to prevent local hot spots. Following this solvent stripping, immediately place the grease in a vacuum chamber to cool.
- 5 - When cooled sufficiently, mill the grease if required.

Large Sample (3 to 6 Pounds)

- Step 1 - Charge appropriate amounts of intermediate, diester, and benzene to vacuum grease kettle.
- 2 - Add 3 methyl glutaric acid in acetone-benzene solution. Maintain stirring.
- 3 - Apply heat and strip solvents to 100°C.
- 4 - Apply 26 inches of vacuum and strip to 150°C.
- 5 - Finish grease by stripping to 195°C. while pulling dry air over grease. Maintain 5 inches of vacuum.

APPENDIX III

SMALL SAMPLE EVALUATION OF PLUROXIN E 231 GREASES

<u>Experiment</u>	<u>Oil Phase</u>	<u>Melting Point °F.</u>	<u>Consistency A.S.T.M. Penetration</u>	<u>Per Cent Con- version</u>	<u>Per Cent Active Gelling Agent</u>	<u>Disp. Ratio</u>
CRB 4-33	Di-2,ethyl hexyl adipate	Below 300	Liquid	60	4	.285
34	Di-2,ethyl hexyl adipate	Below 300	Very heavy	70	7	.285
36A	Di-2,ethyl hexyl adipate	Below 300	Above 350	40	5.5	.55
36B	Di-2,ethyl hexyl adipate	300 +	Approximately 60 200		6.6	.55
37A	Di-2,ethyl hexyl adipate	Below 300	Approximately 60 230		5.5	.55
37B	Di-2,ethyl hexyl adipate	Below 300	Approximately 60 280		4.5	.55
38C	Di-isoctyl azelate	Below 300	Approximately 60 280		5	.39

APPENDIX IV

SMALL SAMPLE EVALUATION OF 3 METHYL GLUTARIC ACID GREASES

Experiment No.	Per Cent Active Gelling Agent	Per Cent Conversion	Shell Micro Penetration	Water Resistance Per Cent Loss	Dropping Point, °F.	Evaporation Per Cent Loss at 300°F.	Oil Separation	Low Temperature Torque Seconds
CRB 4-42A	5	65	Fluid					
CRB 4-42B	5.5	65	Fluid					
CRB 4-42C	6	65	Fluid					
CRB 4-42D	5	75	Fluid					
CRB 4-42E	5.5	75	338					
CRB 4-42F	6	75	180			1.87		
CRB 4-42G	4	80	178					
CRB 4-42H	4.5	80	162	40.0				
CRB 4-42I	5	80	136		490			
CRB 4-42J	5.5	80	135		485			
CRB 4-42K	6	80	148					
CRB 4-42L	4	85	166					
CRB 4-42M	4.5	85	150		500			
CRB 4-42N	5	85	144			1.70		
CRB 4-42O	5.5	85	132	13.3	485		No Loss	0.5
CRB 4-42P	6	85	125					

APPENDIX V

3 METHYL GLUTARIC ACID COUPLED GREASES*

Experiment Number	Dis- persion Ratio	Per Cent A.G.A.	Per Cent DC510-50	Dropping Point, °F.	As Received	PENETRATION		
						60	3,000	After
						Stroke Worked	Stroke Worked	24 Hours Standing
BPSII-132-2	0.2	6	8	226	235	305	310	255
RMTIV-43-1	0.2	6	10	260	285	295	295	260
RMTIV-43-2	0.2	6	12	300	275	300	310	275
RMTIV-43-3	0.2	6	14	446	280	295	300	265
RMTIV-45-2	0.2	6.5	8	168	335	325	330	265
RMTIV-45-3	0.2	6.5	14	410	310	310	310	280
BPSII-138	0.2	7	0	118	350	500+	fluid	325
RMTIV-46-1	0.2	7	8	166	335	315	330	275
RMTIV-46-2	0.2	7	14	228	295	305	305	270
BPSII-123-1	0.3	6	8	244	320	365	365	360
BPSII-123-2	0.3	6	10	450+	335	360	360	355
BPSII-123-3	0.3	6	12	450+	330	370	375	360
BPSII-123-4	0.3	6	14	446	345	360	375	340
BPSII-122-1	0.3	7	8	450+	285	345	350	315
BPSII-122-2	0.3	7	10	450+	305	330	340	305
BPSII-122-3	0.3	7	12	450+	300	330	335	295
BPSII-122-4	0.3	7	14	446	300	335	340	290
BPSII-133-2	0.3	7.5	8	450+	210	280	275	225
BPSII-122-5	0.3	8	8	450+	235	290	305	255
BPSII-122-6	0.3	8	10		250	295	305	260
BPSII-122-7	0.3	8	12		270	295	300	260
BPSII-122-8	0.3	8	14		250	300	300	270
BPSII-125-1	0.35	6.5	8		365	Semi- fluid	Semi- fluid	Semi- fluid
BPSII-125-2	0.35	6.5	10	218	350	385	415	360
BPSII-125-3	0.35	6.5	12	450+	340	385	380	350
BPSII-125-4	0.35	6.5	14	450+	340	375	350	345
BPSII-125-5	0.35	7.0	8	450+	300	355	355	320
BPSII-125-6	0.35	7.0	10	450+	315	340	350	310
BPSII-125-7	0.35	7.0	12	450+	290	330	340	310

APPENDIX V (CONTINUED)

3 METHYL GLUTARIC ACID COUPLED GREASES*

Experiment Number	Dis- persion Ratio	Per Cent A.G.A.	Per Cent DC510-50	Dropping Point, °F.	As Received	PENETRATION		
						60	3,000	After
						Stroke Worked Pen.	Stroke Worked Stability	24 Hours Standing
BPSII-125-8	0.35	7.0	14	450+	300	340	345	310
BPSII-126-5	0.35	7.5	8	450+	285	320	330	285
BPSII-126-6	0.35	7.5	10	450+	275	315	315	260
BPSII-126-7	0.35	7.5	12	450+	295	310	310	270
BPSII-126-8	0.35	7.5	14	450+	290	315	330	285
BPSII-126-1	0.35	8	8	450+	250	315	320	265
BPSII-126-2	0.35	8	10	450+	270	310	315	275
BPSII-126-3	0.35	8	12	450+	260	310	325	285
BPSII-126-4	0.35	8	14	450+	275	310	320	265
BPSII-110-1	0.4	7	8		325	360	390	335
BPSII-110-11	0.4	7	10		320	365	370	345
BPSII-110-12	0.4	7	12		320	355	370	335
BPSII-110-13	0.4	7	14		310	350	360	340
BPSII-110-2	0.4	8	8		320	345	370	335
BPSII-110-8	0.4	8	10		295	345	350	325
BPSII-110-9	0.4	8	12	458	295	345	350	315
BPSII-110-10	0.4	8	14		310	340	345	325
BPSII-117-1	0.4	8.5	8	450+	265	325	340	290
BPSII-117-2	0.4	8.5	10	450+	250	320	325	290
BPSII-117-3	0.4	8.5	12	450+	245	315	325	270
BPSII-117-4	0.4	8.5	14	450+	265	325	325	270
BPSII-110-17	0.4	9	8		245	315	315	215
BPSII-110-18	0.4	9	10		245	300	310	220
BPSII-110-19	0.4	9	12		250	295	305	245
BPSII-110-20	0.4	9	14		245	295	305	235
BPSII-110-3	0.45	7	8		345	395	Semi- fluid	Semi- fluid
BPSII-110-14	0.45	7	10		340	380	405	355
BPSII-110-15	0.45	7	12		335	390	405	365
BPSII-110-16	0.45	7	14	450+	330	370	385	360
BPSII-110-4	0.45	8	8		315	395	Semi- fluid	Semi- fluid

APPENDIX V (CONTINUED)
3 METHYL GLUTARIC ACID COUPLED GREASES*

Experiment Number	Dis- persion Ratio	Per Cent A.G.A.	Per Cent DC510-50	Dropping Point, OF.	PENETRATION			
					As Received	60		After 24 Hours
						Stroke Worked Pen.	3,000 Stroke Worked Stability	
BPSII-110-5	0.45	8	10		290	370	375	320
BPSII-110-6	0.45	8	12		300	365	375	295
BPSII-110-7	0.45	8	14		300	365	390	330
BPSII-110-21	0.45	9	8		265	340	345	300
BPSII-110-22	0.45	9	10		275	345	345	300
BPSII-110-23	0.45	9	12		290	335	340	310
BPSII-110-24	0.45	9	14		285	330	340	295
BPSII-127-1	0.45	9.5	8	450+	250	310	315	265
BPSII-127-2	0.45	9.5	10		265	305	305	260
BPSII-127-3	0.45	9.5	12	450+	265	305	300	250
BPSII-127-4	0.45	9.5	14	450+	260	285	300	260
BPSII-110-33	0.5	8	8	450+	335	410	Semi- fluid	Semi- fluid
BPSII-110-34	0.5	8	10		320	385	405	345
BPSII-110-35	0.5	8	12	450+	325	375	385	345
BPSII-110-36	0.5	8	14		340	365	380	325
BPSII-110-25	0.5	9	8		285	345	360	325
BPSII-110-26	0.5	9	10	450+	300	350	350	320
BPSII-110-27	0.5	9	12		295	345	350	310
BPSII-110-28	0.5	9	14	360	295	345	350	330
BPSII-110-29	0.5	10	8		270	355	350	310
BPSII-110-30	0.5	10	10		275	330	330	290
BPSII-110-31	0.5	10	12		275	320	335	290
BPSII-110-32	0.5	10	14		290	325	330	300
BPSII-138-1**	0.4	8.5	0	230	220	325	330	300
RMTIV-47-1**	0.4	8.5	8	450+	220	305	315	255
RMTIV-47-2**	0.4	8.5	14	450+	245	300	295	255
BPSII-136-1***	0.4	8.5	0	100	290	380	fluid	fluid
RMTIV-45-5***	0.4	8.5	8	450+	245	330	345	290
RMTIV-45-6***	0.4	8.5	14	450+	265	315	320	275

* All greases 85 per cent conversion.

** 60 per cent post dodecylbenzene sulfonate greases.

*** 40 per cent post dodecylbenzene sulfonate greases.

APPENDIX VI

MATERIALS INEFFECTIVE AS THIXOTROPY INHIBITORS

Glycols

Polypropylene glycols of average M.W. = 150, 425, 1025, 2025

Methoxy polyethylene glycol average M.W. = 315,550

Polyglycol E 600

Dibutoxy tetraglycol

Dimethoxy tetraethylene glycol

Tetraethylene glycol dichloride

Triglycol dichloride

Esters

Flexol Plasticizers 8HP, DOP, 2GB (Carbide and Carbon)

Santicizers M-17, 107 (Monsanto)

Dibutyl phthalate

Dioctyl phthalate

Miscellaneous

Polyethylenes

Polybutenes

170 pale oil

Tributyl phosphate

Tricresyl phosphate

Amine 220 (Carbide and Carbon)

Dow Corning Silicone Fluid DC 500

GE Silicone Fluid No. 81451

Lithium epoxy oleate

Lithium dihydroxy oleate

APPENDIX VII

EFFECT OF ADDITIVES ON 3 METHYL GLUTARIC ACID COUPLED GREASES*

Experiment Number	Dis- persion Ratio	Per Cent A.G.A.	Per Cent DC510-50	Per Cent Acryloid 710	Water Resistance Per Cent Loss	Low Temp. Torque	Dropping Point	Evapora- tion Per Cent Loss	PENETRATION			
									As Received	60 Strokes Worked	3,000 Strokes Worked	After 24 Hours Standing
BFSII-128-3	.4	8	8	5			450+		275	315	325	280
BFSII-128-4	.4	8	8	10			450+		280	320	335	295
BFSII-128-5	.4	8	14	5			450+		290	330	340	310
BFSII-128-6	.4	8	14	10			450+		295	340	345	320
BFSII-128-7	.4	8	0	10	41.6		450+		265	305	320	290
BFSII-128-8	.4	8	8	3			450+		280	320	325	280
BFSII-129-3	.3	8	8	5	43.3	.2 sec.	450+	.26	220	260	260	220
BFSII-129-4	.3	8	8	10	63.3	1.2 sec.	450+	.44	230	265	260	235
BFSII-129-5	.3	8	14	5	40.0		442	.29	220	260	245	230
BFSII-129-6	.3	8	14	10	43.3		430	.41	245	265	270	250
RMT-IV-29-1	.4	9	10	3	74.6	.25 sec.	450+		225	295	305**	250
RMT-IV-29-2	.4	9	10	3% Esso Acto 630	36.8, 34.0	1.4 sec.	450+		205	300	305***	245
BFSII-129-2	.3	8	-	-	8.0, 11.8				205	260	265	200

* All greases 85 per cent conversion.

** Had penetration of 300 after 50,000 double strokes.

*** Had penetration of 320 after 50,000 double strokes.

APPENDIX VIII

EFFECT OF FINISHING TEMPERATURE ON GREASE PROPERTIES

OBSERVATIONS

Experiment Number	Initial 195°C. Treatment	Reworked Plus 195°C. Second Treatment	On Cooling	ATMOSPHERIC EXPOSURE		Appearance of Sample in Sealed Jar
				72 Hours	192 Hours	
BPS II-83A				Definite Set		
BPS II-83A	Crumbly	Semifluid	Original Consistency	Original Consistency	Definite Set	Original Consistency
BPS II-85B				Original Consistency	Definite Set	
BPS II-85B	Crumbly	Semifluid	Original Consistency	Original Consistency	Definite Set	Original Consistency
BPS II-85D				Slight Set		
BPS II-85D	Crumbly	Original Consistency	Original Consistency	Original Consistency	Definite Set	Original Consistency
BPS II-96A				Original Consistency	Slight Set	
BPS II-96A	Crumbly	Original Consistency	Original Consistency	Original Consistency	Original Consistency	Original Consistency
BPS II-83A	7 per cent AGA, 85 per cent conversion, stripped to 150°C. BPS II-83A + Sulfonate intermediate (95 BM) to base number of 15, stripped to 150°C. 92 per cent BPS II-83A + 8 per cent DC 510-50, stripped to 150°C. 86 per cent BPS II-83A + 9 per cent DC510-50 + 5 per cent Esso Acto 630, stripped to 150°C.					
BPS II-85B						
BPS II-85D						
BPS II-96A						

APPENDIX IX

UNSUITABLE SET INHIBITORS

<u>Additive</u>	<u>Level in Final Grease</u>	<u>Observations</u>
<u>Oxidation Inhibitor</u>		
Phenothiazine	1 per cent	No effect
<u>Hydrogen Bonding Agents</u>		
Glycerin	1 per cent	Cloudy, bleeds
Glycerin	.05 per cent	Cloudy, bleeds
Mannitol	1 per cent	Particles of undispersed solid remain
<u>Ucon Lubricants</u>		
LB1715	1 per cent	Cloudy, not work stable
50HB2000	1 per cent	Cloudy, not work stable
50HB5100	1 per cent	Cloudy, not work stable
75H490	1 per cent	Cloudy, not work stable
75H1400	1 per cent	Cloudy, not work stable
75H90000	1 per cent	Cloudy, not work stable
Polyethylene glycol 1025	1 per cent	No effect
Polyethylene glycol 2025	1 per cent	No effect
Monobutyl amine	1 per cent	Hydrolysis occurs with all amines
2-ethyl hexyl amine	1 per cent	
Di-2 ethyl hexyl amine	1 per cent	
Tetraethylene pentamine	1 per cent	
<u>Sulfonate Fluidizing Agents</u>		
Diethyl phthalate	1 per cent	No effect
Surfynol 104	4.7 per cent	No effect
Sulfonate intermediate to base No. of 5		No effect
Naphthenic intermediate to base No. of 7		No effect

APPENDIX X

EXHIBIT "A"

Development and evaluation of a grease with high load carrying capacity that is operational over a -100° to 350°F. temperature range. There is no restriction on the materials to be used in making this grease. An oil must be found with good lubricating properties that is stable over this temperature range and with low volatility at the upper temperature limit. A good gelling agent stable over the temperature range is also needed. The grease must possess oxidation stability, permit operation of low torque aircraft equipment at -100°F., provide adequate lubrication over the temperature range of -100°F. to 350°F., and supply adequate protection against corrosion.

Requirements for a -100° to 350°F. Grease

Test and Method	<u>Requirement</u>
1. Oxidation Stability Spec. VV-L-791, Method 345.3	Pressure drop shall not exceed: 5 p.s.i. in 100 hours 25 p.s.i. in 500 hours
2. Dropping Point Spec. VV-L-791, Method 142.1	> 375°F.
3. Worked Penetration Spec. VV-L-791, Method 31.1	> 260, < 340
4. Dirt Spec. VV-L-791, Method 300.5	The grease shall not contain dirt or other foreign particles exceeding the following limits: 7,500 per cc. of 25μdiameter or above 1,600 per cc. of 75μdiameter or above None of 125μdiameter or above
5. Bomb Copper Corrosion Spec. MIL-G-3278, 4.2.2.3.	Pressure drop shall not exceed 0.5 p.s.i. in 20 hours. No decomposition of the grease as evidenced by discoloration in the vicinity of the copper strip or appreciable stain or corrosion beyond that obtained in a blank test under the same conditions without grease. A slight change in the color of the grease, not green or dark brown, is acceptable.

APPENDIX X (CONTINUED)

EXHIBIT "A" (CONTINUED)

<u>Test and Method (Continued)</u>	<u>Requirement (Continued)</u>
6. Water Resistance a. Water Washing Spec. VV-L-791 Method 325.2	Not more than 20 per cent of the grease shall be washed from the bearing when tested.
b. Water Immersion Spec. MIL-G-3278, 4.2.2.4	No cloudiness or other evidence of emulsification of the grease.
7. Evaporation Spec. VV-L-791, Method 35.1	Grease shall not lose more than 2.0 per cent of its weight in 22 hours.
8. Oil Separation Spec. VV-L-791 Method 32.1	Grease shall not lose more than 5 per cent of its weight in 30 hours
9. Apparent Viscosity Spec. VV-L-791, Method 30.6	Viscosity of the grease shall not exceed 15,000 poises at a shear rate of 20 reciprocal seconds at -100°F.
10. Gear Wear Test Spec. MIL-G-3278, 4.2.2.8	The brass gear of a helical gear set shall not wear more than 2.5 mg. per 1,000 cycles under a 5-pound load nor more than 3.5 mg. per 100 cycles under a 10-pound load.
11. Worked Stability Spec. VV-L-791, Method 31.3	375 after working 100,000 double strokes.
12. Low Temperature Torque Spec. MIL-G-7421, 4.4.2.1	A 204 Conrad-type 8-ball bearing lubricated with the grease shall turn its first complete revolution in each direction in not more than 5 seconds at -100°F.
13. High Temperature Performance, Spec. VV-L-791, Method 33.1	The grease shall lubricate a 204 Conrad-type 8-ball bearing satisfactorily for a minimum of 600 hours at 350°F.
14. Humidity Corrosion Test Spec. MIL-G-4343, 4.3.2.3	Each of the two tested bearings must have a numerical rating of 2 or less.

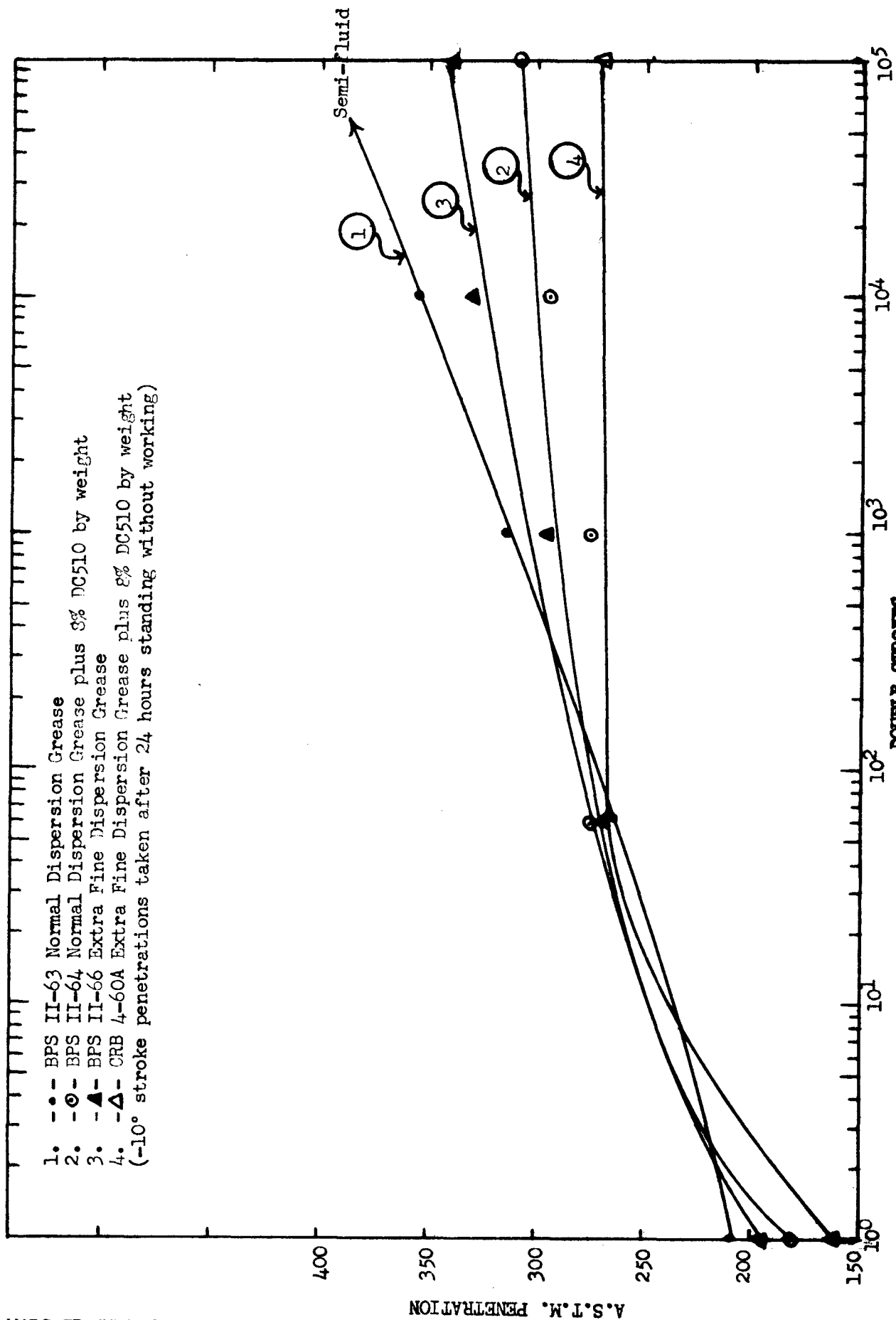


FIGURE 1 EFFECT OF PARTICLE SIZE ON WORKED STABILITY

--●-- Base Grease 7% active gelling agent 85% conversion
 --○-- 1% DC 510-50 by weight additional
 --△-- 3% DC 510-50 by weight additional
 --▲-- 6% DC 510-50 by weight additional
 --◻-- 9% DC 510-50 by weight additional
 (-100 stroke penetration taken after 24 hours standing without working)

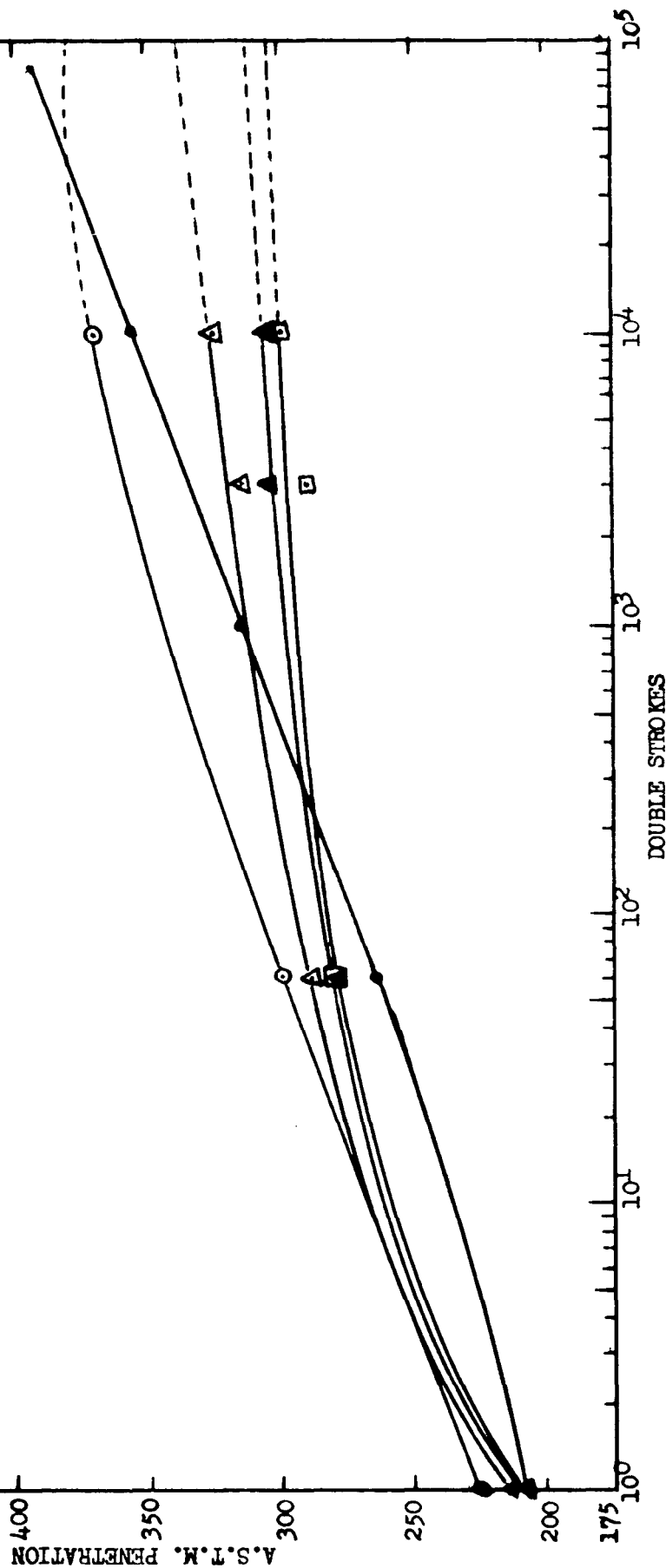


FIGURE II EFFECT OF DC510 SILICONE FLUID ON WORKED STABILITY

7.0% AGA, 0% DC510

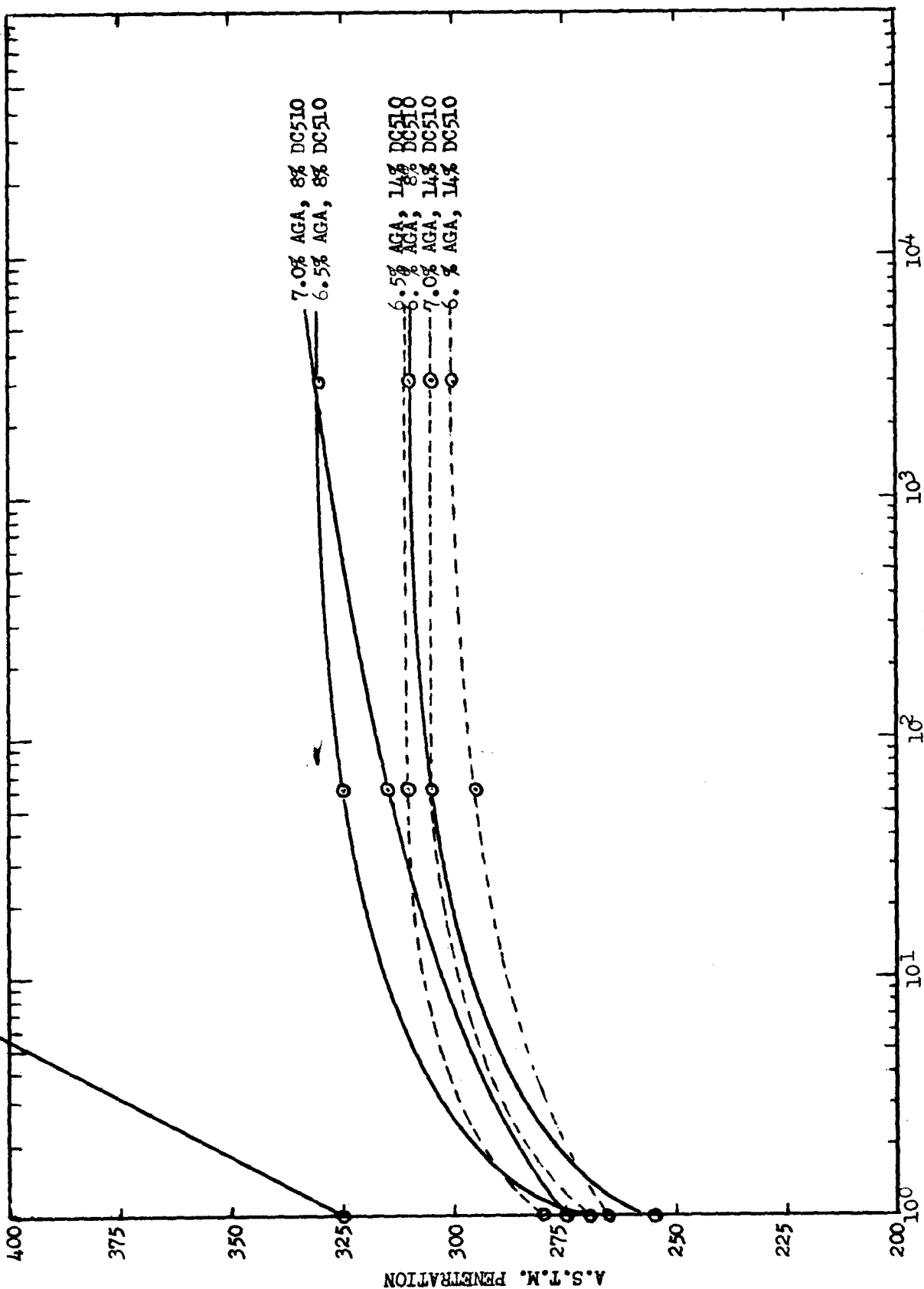


FIGURE III EFFECT OF VARYING PER CENT ACTIVE GELLING AGENT AND PER CENT SILICONE AT A CONSTANT DISPERSION RATIO (0.2)

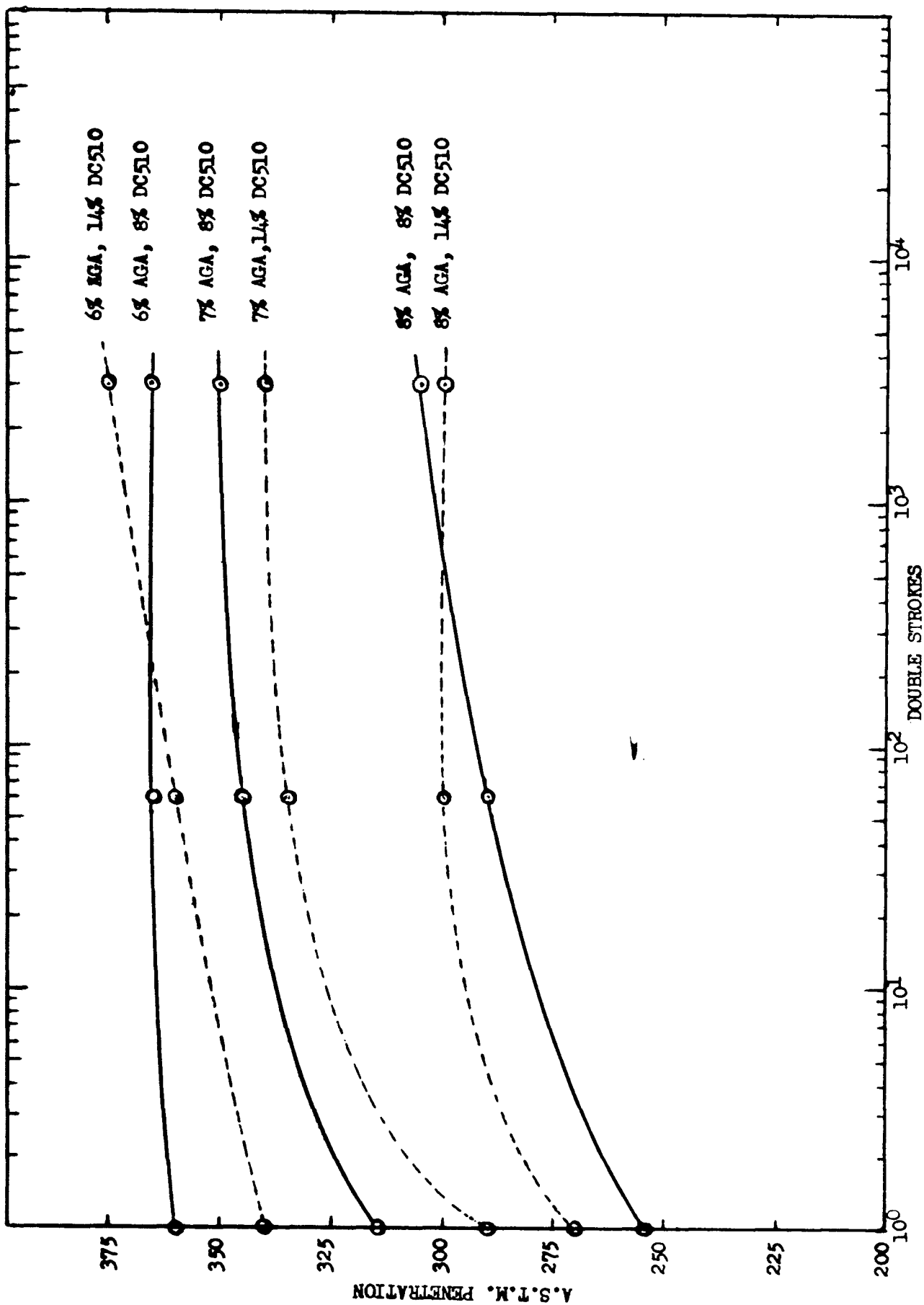


FIGURE IV EFFECT OF VARYING PER CENT ACTIVE GELLING AGENT AND PER CENT SILICONE AT A CONSTANT DISPERSION RATIO (0.3)

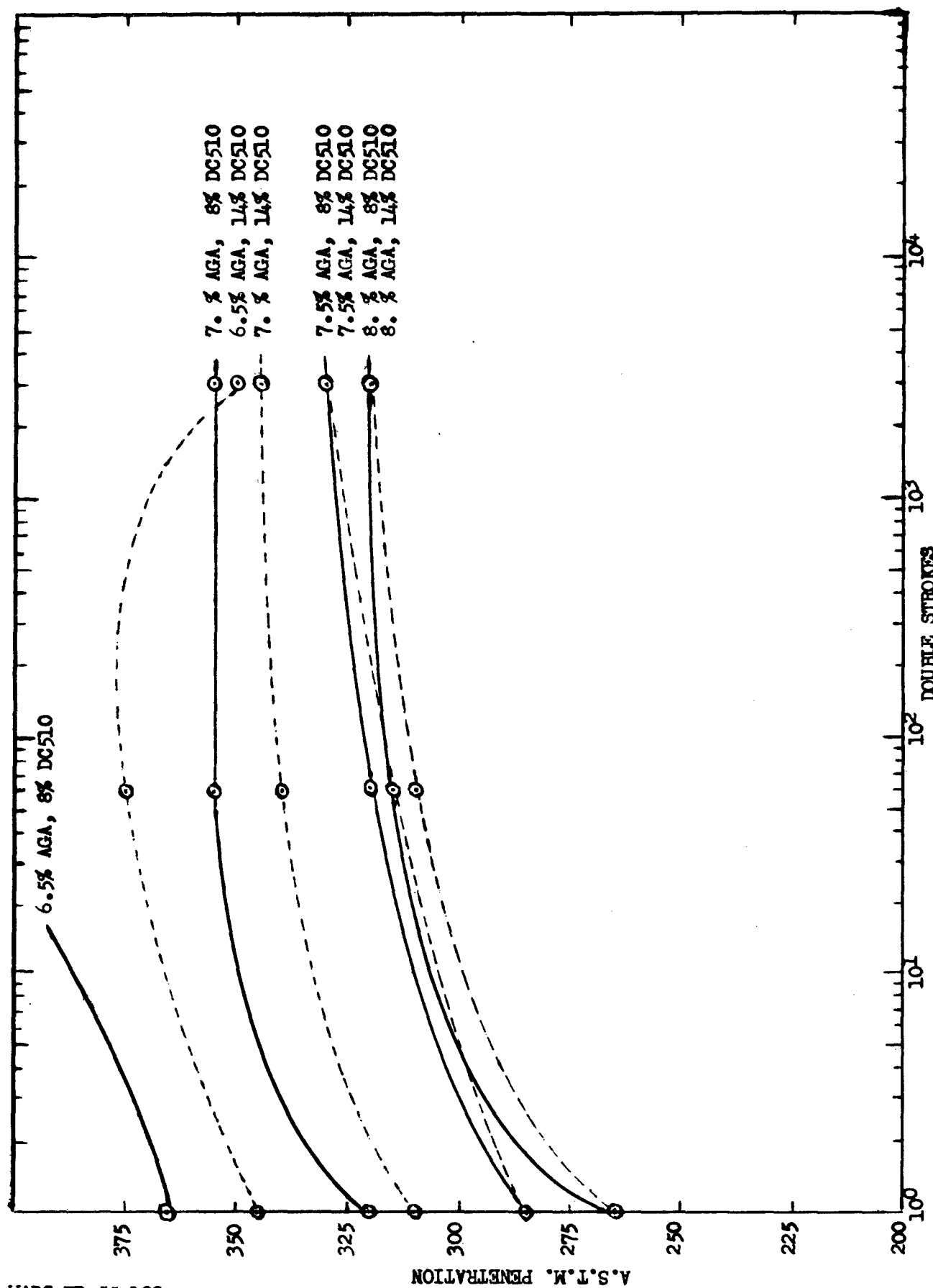


FIGURE V EFFECT OF VARYING PER CENT ACTIVE GELLING AGENT AND PER CENT SILICONE AT A CONSTANT DISPERSION RATIO (0.35)

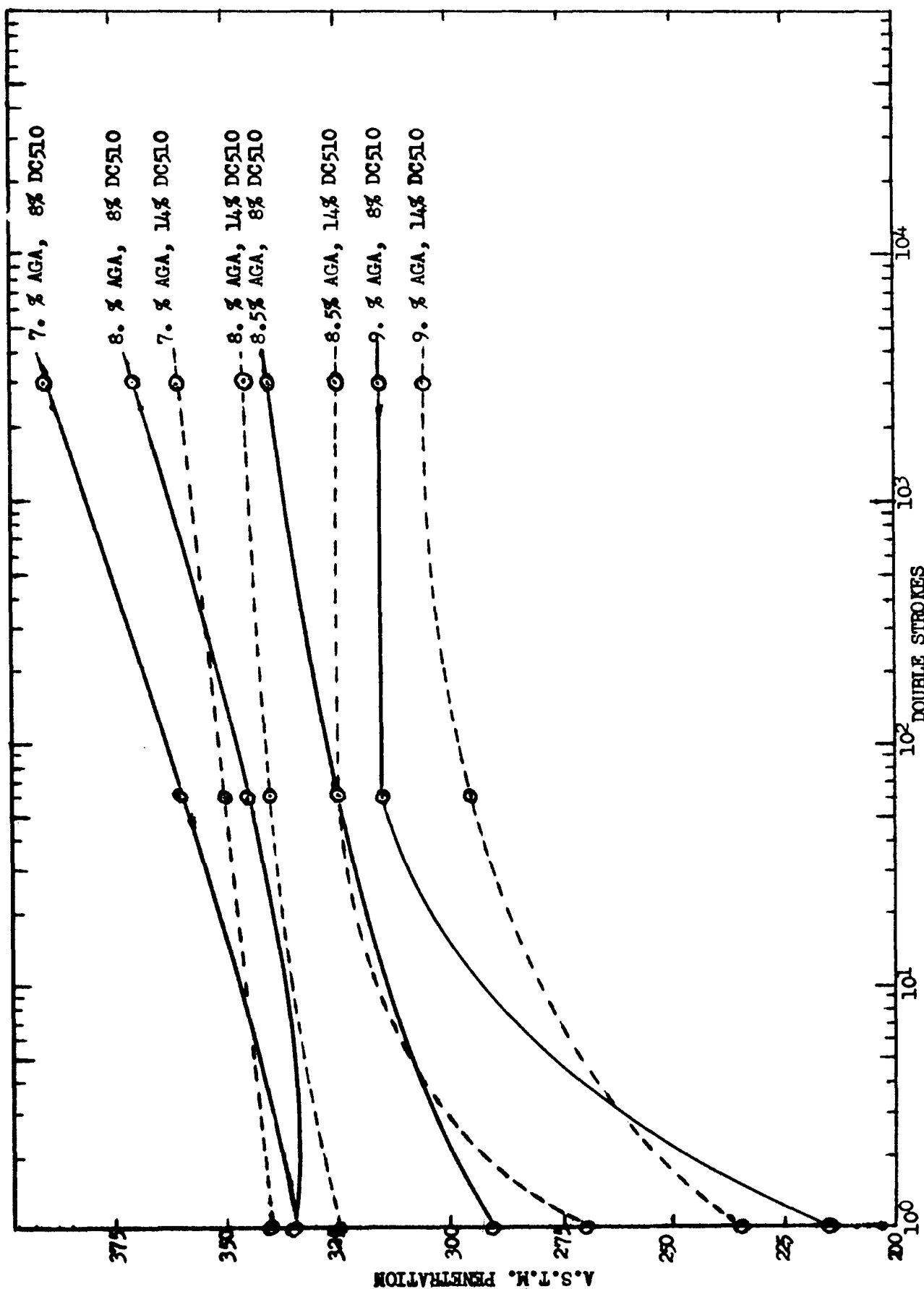


FIGURE VI EFFECT OF VARYING PER CENT ACTIVE GELLING AGENT AND PER CENT SILICONE AT A CONSTANT DISPERSION RATIO (0.4)

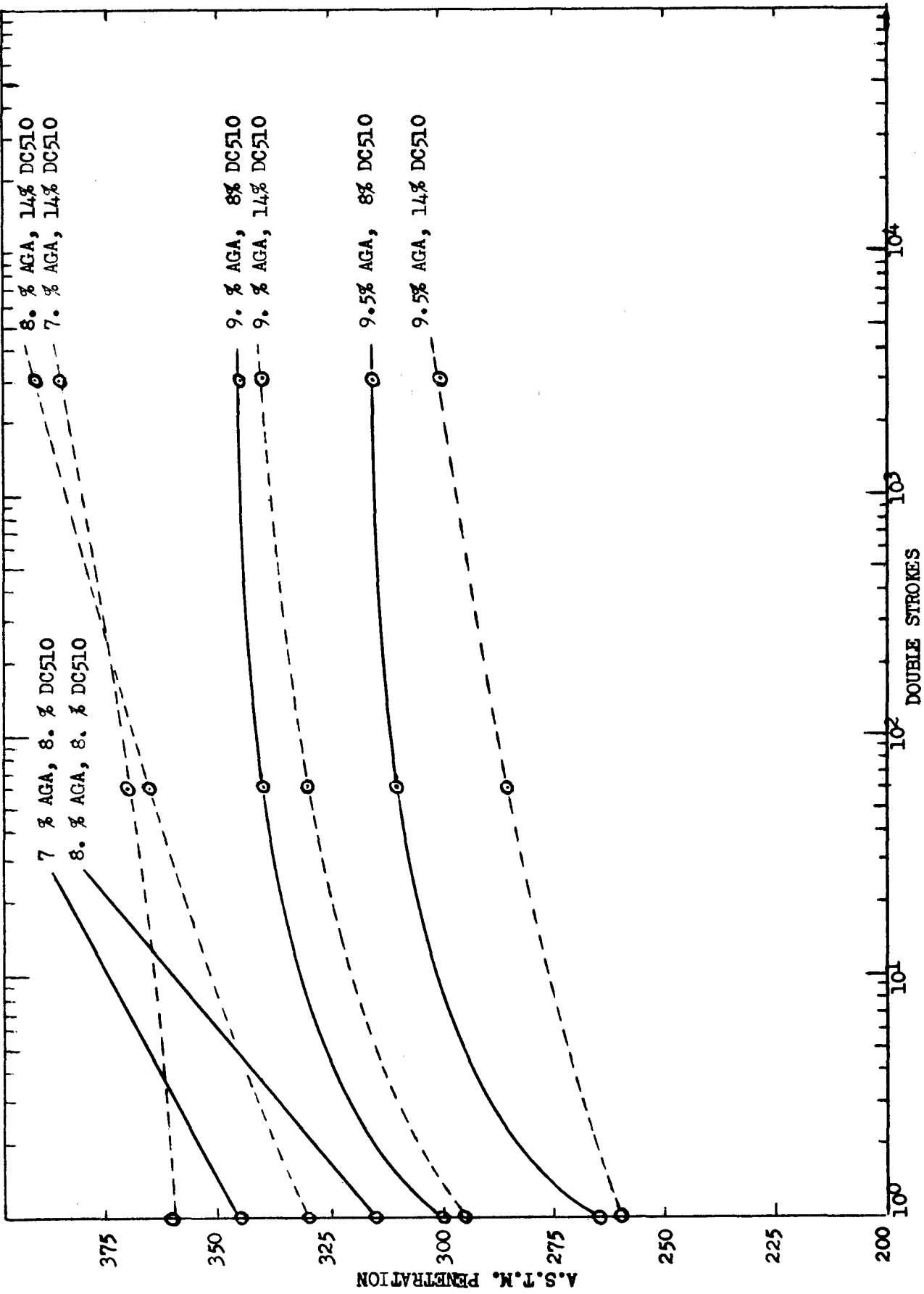


FIGURE VII. EFFECT OF VARYING PER CENT ACTIVE GELLING AGENT AND PER CENT SILICONE AT A CONSTANT DISPERSION RATIO (0.45)

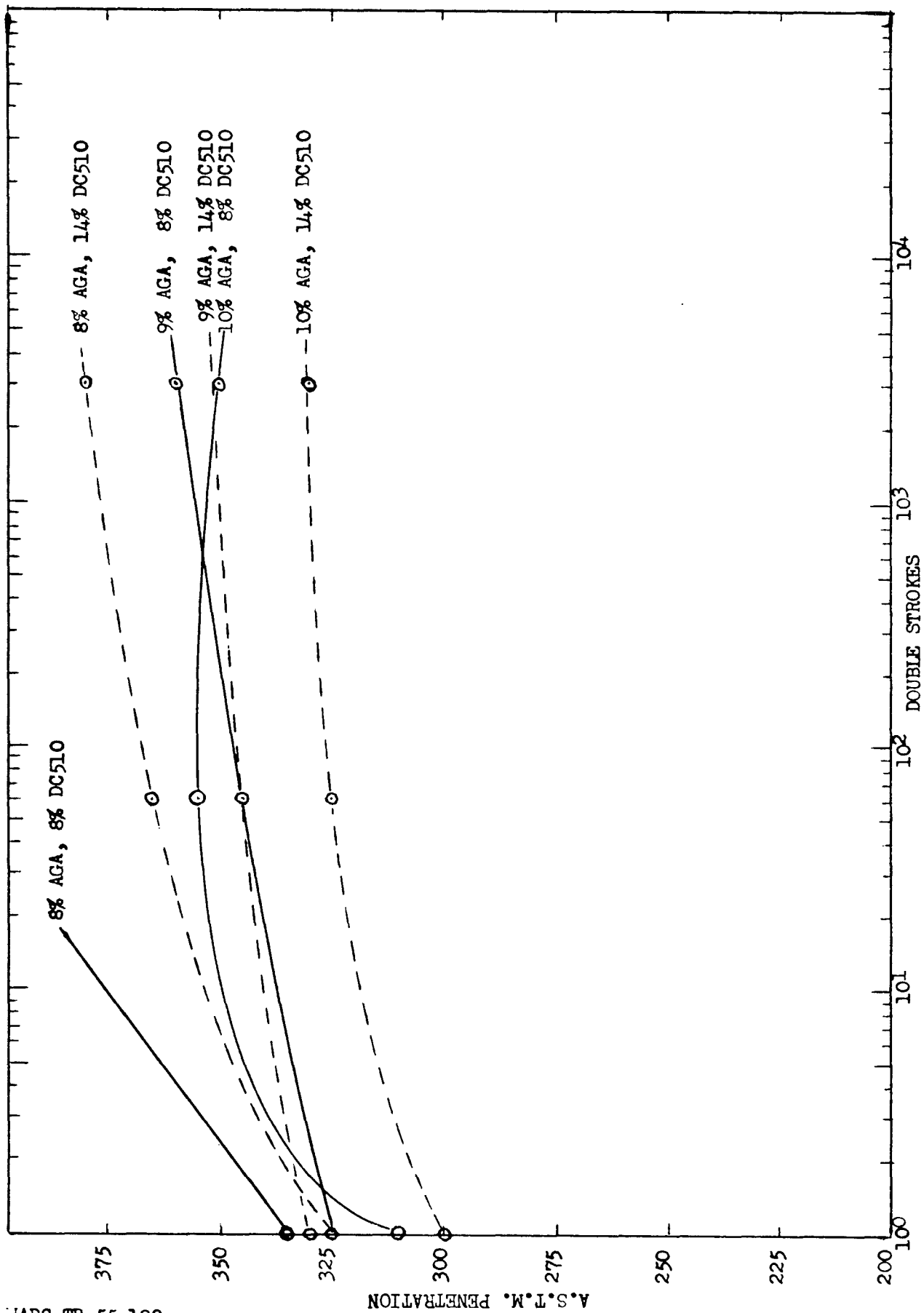


FIGURE VIII EFFECT OF VARYING PER CENT ACTIVE GELLING AGENT AND PER CENT SILICONE AT A CONSTANT DISPERSION RATIO (0.5)

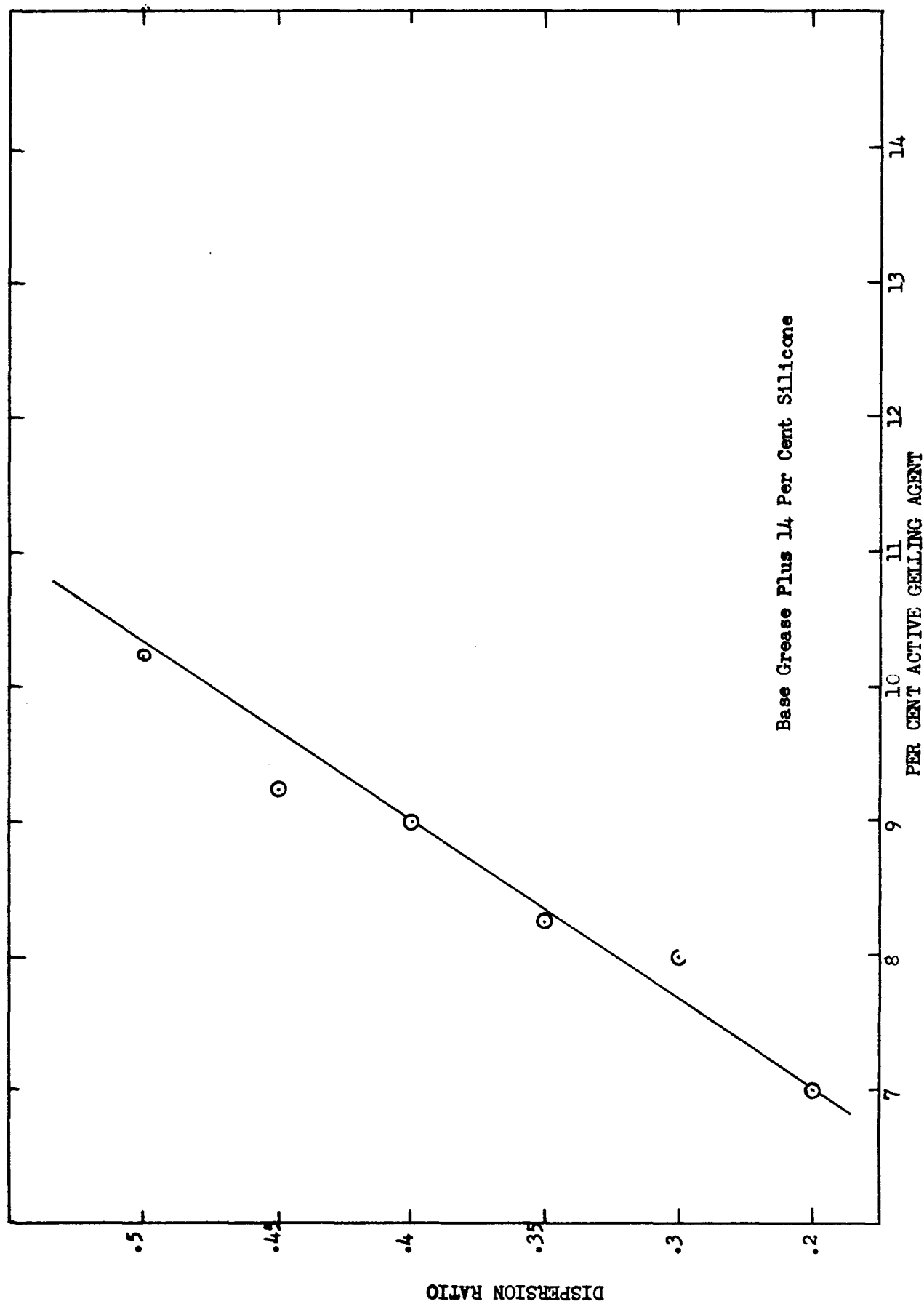


FIGURE IX DISPERSION RATIO - ACTIVE GELLING AGENT
REQUIREMENTS FOR 300 PENETRATION GREASE

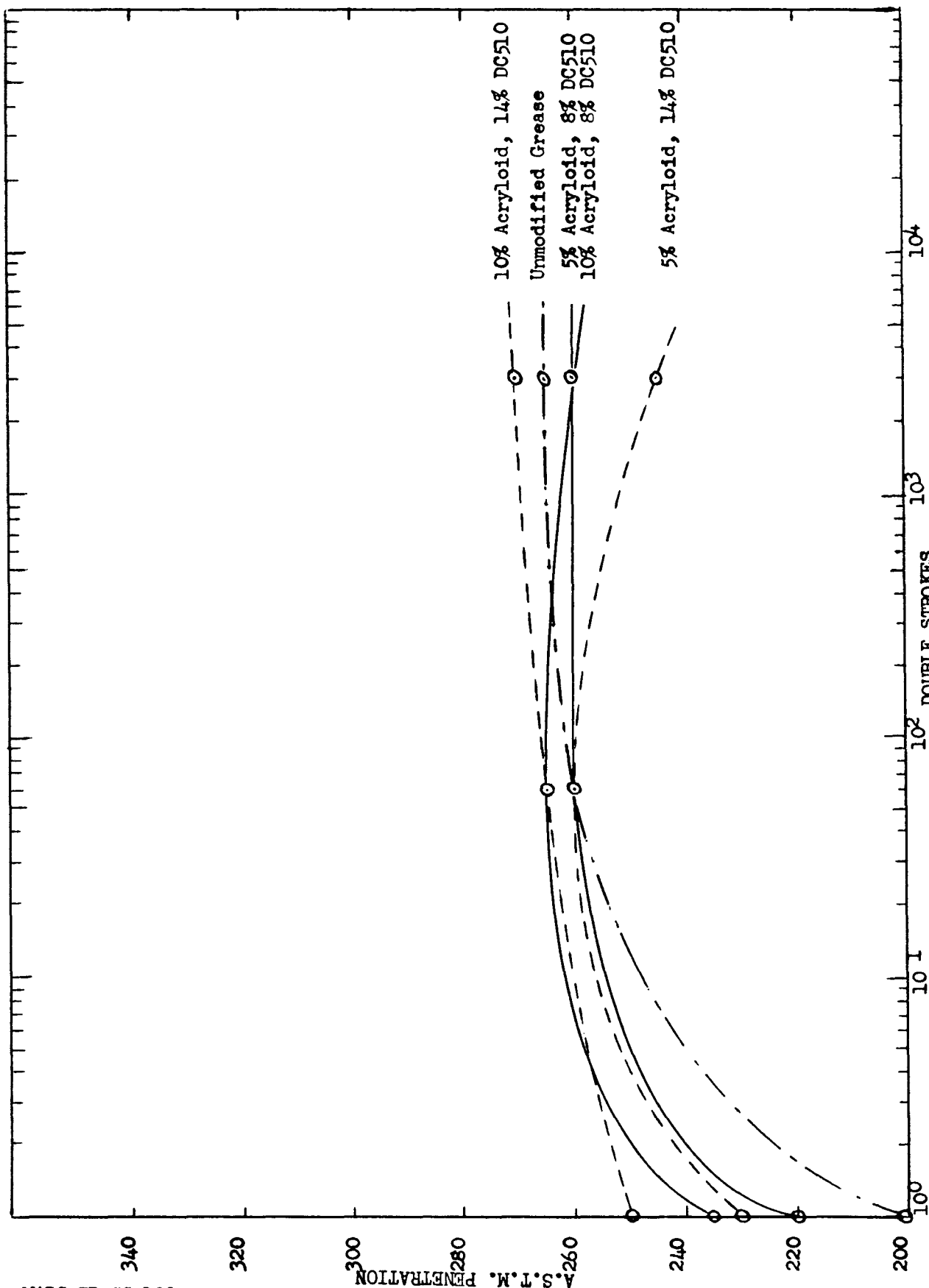


FIGURE X EFFECT OF VARYING PER CENT ACRYLOID AND PER CENT SILICONE ON A CONSTANT ACTIVE GELLING AGENT (8 PER CENT) AND DISPERSION RATIO (0.3) GREASE

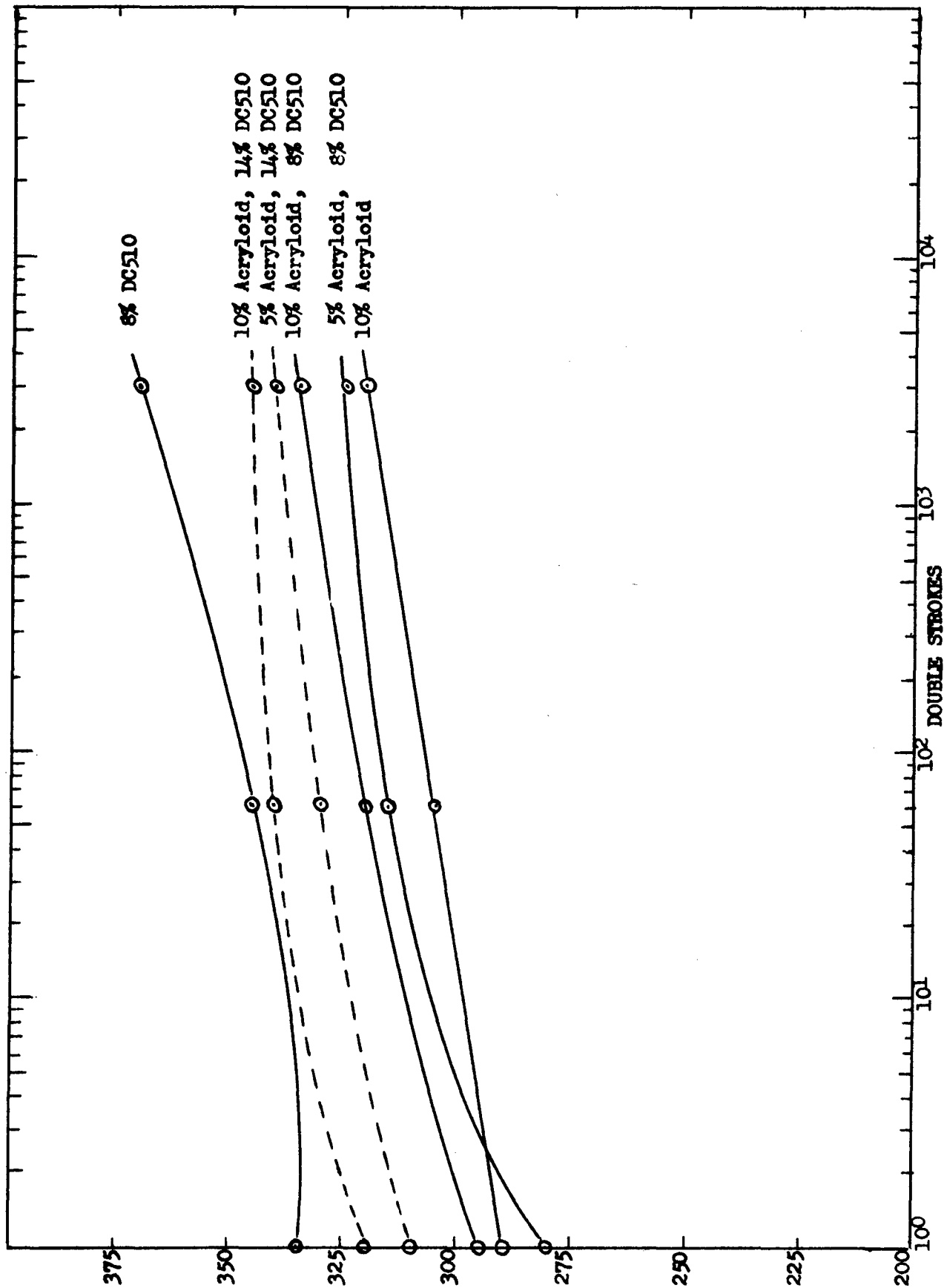


FIGURE XI EFFECT OF VARYING PER CENT ACRYLOID AND PER CENT SILICONE ON A CONSTANT ACTIVE GELLING AGENT (8 PER CENT) AND DISPERSION RATIO (0.4) GREASE

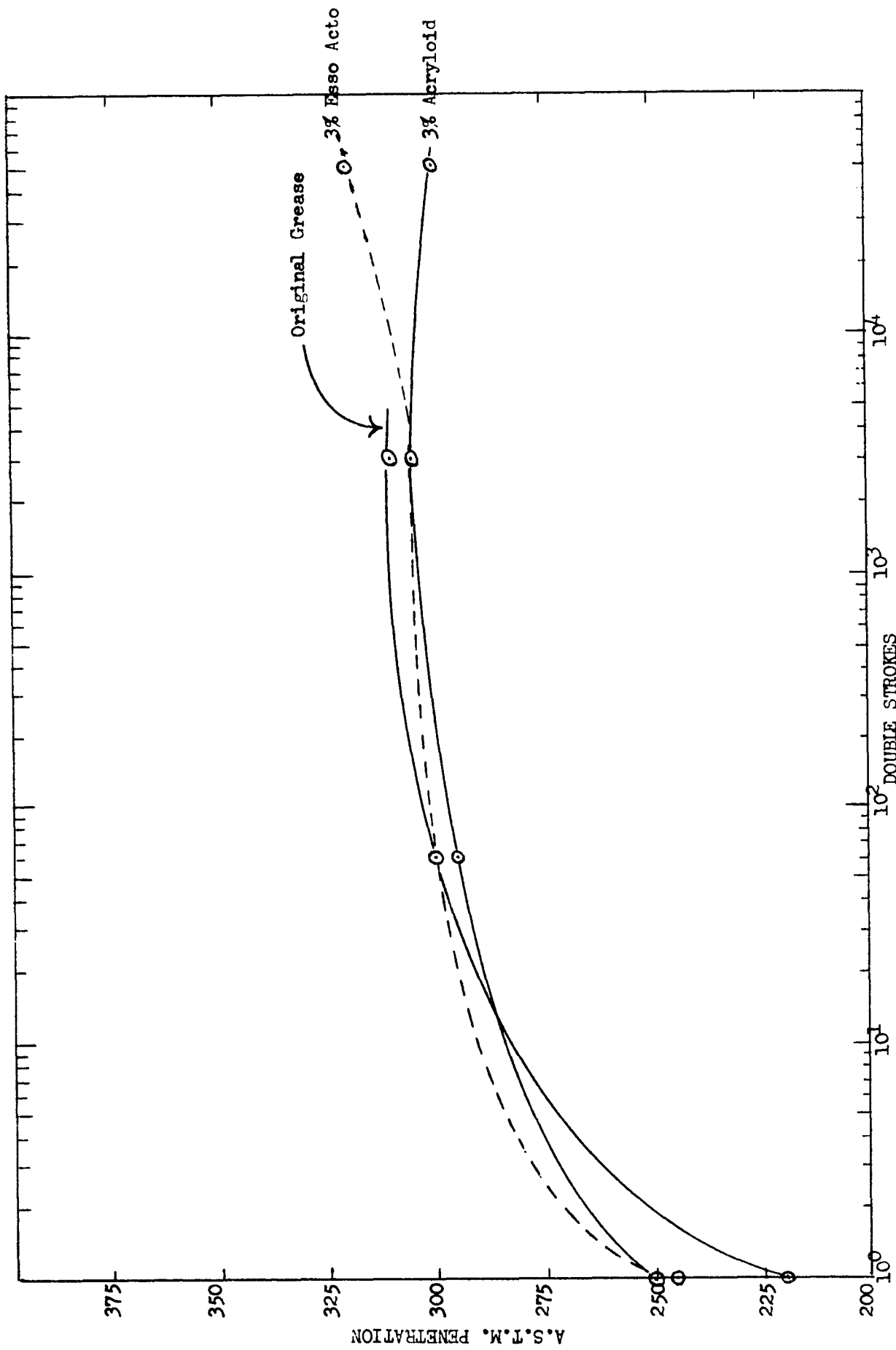


FIGURE XII EFFECT OF ACRYLOID AND ESSO ACTO ON A 0.4 DISPERSION RATIO,
9 PER CENT ACTIVE GELLING AGENT, 10 PER CENT SILICONE GREASE

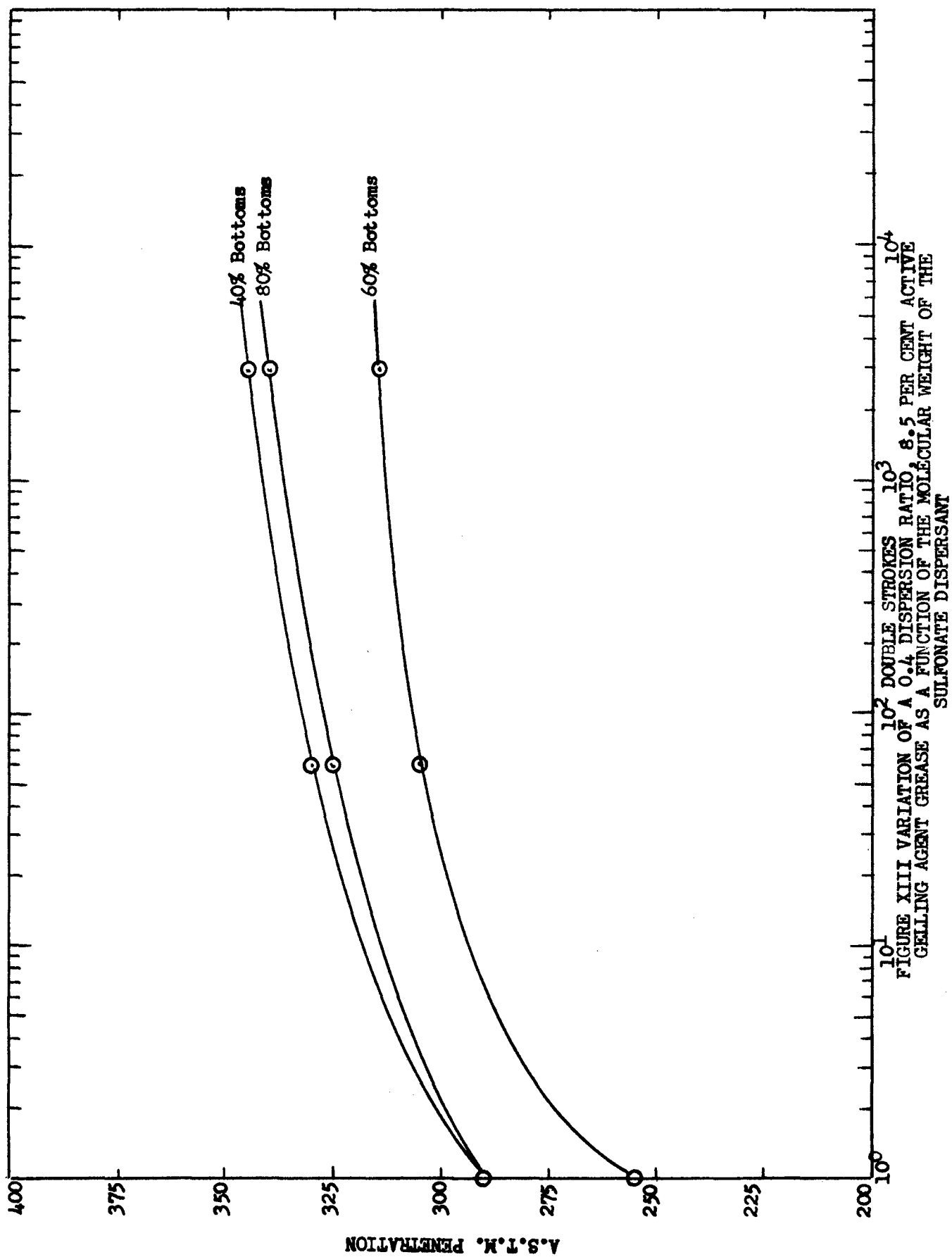


FIGURE XIII VARIATION OF A 0.4 DISPERSION RATIO, 8.5 PER CENT ACTIVE GELLING AGENT GREASE AS A FUNCTION OF THE MOLECULAR WEIGHT OF THE SULFONATE DISPERSANT